VOL. XLIV. NOVEMBER, 1910. NO. 5.

AMERICAN CHEMICAL JOURNAL

[Contributions from the Chemical Laboratory of Harvard College.]

FUROYLACETIC ESTER AND THE FURYLPYRAZOLONES.[1]

[THIRD PAPER.]

BY HENRY A. TORREY AND J. E. ZANETTI.

INTRODUCTION.

Since the discovery of acetacetic ester by Geuther in 1863,[2] many compounds have been prepared similar to it in general structure but having various radicals in the place of the methyl group, and as the reactions and ring formations due to the $—CO.CH_2.COOC_2H_5$ group are exhibited by all of them to a greater or lesser degree, they have an important place in synthetic work.

Furoylacetic ester, $C_4H_3OCOCH_2COOC_2H_5$, prepared by Bouveault,[3] is of great interest to this laboratory, as it forms part of the furfurane series so long investigated by the late Professor Henry Barker Hill.

Furoylacetic ester had been but little investigated before its study was undertaken by us. But two chemists, M. M.

[1] The work described in this paper formed part of a thesis presented to the faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by J. E. Zanetti. The experimental work was done under the direction of Professor H. A. Torrey, but as the paper was written after his death it did not have the benefit of his revision.—C. L. J.

[2] Jahres. d. Chem., **1863**, 323.

[3] Compt. rend., **125**, 1186. Bull. soc. chim., [3] **25**, 440.

Bouveault and S. S. Sandelin, had done any work upon it and this was confined to the synthesis of the ester and the preparation of three of its derivatives. Bouveault was the first to publish his work on the ester in 1899,[1] but did so only very briefly at the end of a communication to the Académie des Sciences on α-acetylfurfurane, which he had synthesized by decomposing the ester with dilute sulphuric acid. His paper evidently escaped Sandelin's notice, for the following year that author repeated Bouveault's work step by step and published his results[2] without mentioning Bouveault's name. Sandelin not only prepared the furylmethyl ketone, or α-acetylfurfurane, as Bouveault called it, but also the copper salt of the ester and its phenylhydrazine derivative, to which he ascribed the formula of a pyrazolone. Bouveault published a second paper[3] a year afterwards, calling attention to his first paper and confirming Sandelin's work without extending it. As far as we have been able to ascertain, no further work was done on furoylacetic ester until the present research was begun in the fall of 1905. Some of our earlier results we have already published.[4]

The objects of this research were the determination of the influence of the furyl group, both in the ester and in its pyrazolone derivatives, and the synthesis of a substance analogous to antipyrine containing the furyl group that possibly might have therapeutic value. The pyrazolone derivatives are dealt with in the second part of this paper. The first part concerns itself with the ester and its derivatives.

PART I. FUROYLACETIC ESTER.

The preparation of this ester, according to Sandelin's method, was described by us in our first paper,[5] in which we stated that our best yields were obtained by using small quantities of material, 15 grams of ethyl pyromucate and 20 grams of ethyl acetate. By using the sodium in the form of wire, however, we have found it possible to use large quantities of

[1] Compt. rend., *loc. cit.*
[2] Ber. d. chem. Ges., **33**, 492.
[3] Bull. soc. chim., [3] **25**, 435.
[4] This Journal, **31**, 539. J. Am. Chem. Soc., **30**, 1241.
[5] This Journal, **31**, 539.

material and to complete the reaction in three hours, while Bouveault[1] continued the reaction during 24 hours, and Sandelin[2] heated the mixture 7 hours after the sodium had been dissolved. Conclusive proof that the furfurane group suffers no reduction in the course of this reaction is furnished by the formation of the potassium salt of pyromucic acid from the ester by means of a concentrated solution of potassium hydroxide.

Furoylacetic ester has a slightly acid reaction and forms well-defined salts, although it does not remain dissolved in either sodic or potassic hydroxides, but this is because the potassium and sodium salts are fairly insoluble in water and separate out of the alkaline solutions when this is mixed with the ester. Dilute ammonia, however, dissolves it readily. This ester also gives a red color with ferric chloride, in alcohol solution, similar to that of acetacetic and benzoylacetic esters.[3]

Although Schiff[4] finally succeeded in preparing what appears to be the oxime of acetacetic ester by the action of hydroxylamine hydrochloride on a mixture of acetacetic ester and aniline, it is very unstable, readily splitting off a molecule of alcohol and forming methylisoxazolone, the compound that Hantzsch[5] obtained some years before in his study of the action of hydroxylamine on acetacetic ester. From benzoylacetic ester and hydroxylamine neither Claisen and Fedel[6] nor Hantzsch[7] succeeded in isolating the oxime, but obtained instead an isoxazolone. In the case of furoylacetic ester we found no difficulty in isolating the oxime when a mixture of sodium acetate and hydroxylamine hydrochloride was used, and, in striking contrast with the similar compound mentioned above, it is stable enough to be crystallized unchanged from weak alcohol. At the same time the isoxazolone is easily obtained by allowing the hydroxylamine to act on the

[1] Compt. rend., **125**, 1186.
[2] Ber. d. chem. Ges., **33**, 492.
[3] Wislicenus: *Ibid.*, **33**, 2838. Baeyer and Perkin: *Ibid.*, **16**, 2129.
[4] *Ibid.*, **28**, 2731.
[5] *Ibid.*, **24**, 497.
[6] *Ibid.*, **24**, 141.
[7] *Ibid.*, **24**, 502.

ester in neutral or weakly alkaline solutions or by warming the oxime with dilute alkalies.

Hantzsch[1] accounted for the instability of these oximes by considering them from a stereoisomeric point of view. On account of the ease of isoxazolone formation, and since neither in the case of acetacetic ester nor in that of benzoylacetic ester could isomeric oximes be isolated, he assumed that in these cases only the *syn*-oximes,

$$\begin{matrix} R.C.CH_2COOC_2H_5 \\ \| \\ NOH \end{matrix},$$

existed, the phenomenon being accounted for by considering the hydroxyl group more strongly attracted by the $—CH_2COOC_2H_5$ group than by the R group.[2] The stability of the oxime of furoylacetic ester would depend, according to these considerations, on the attraction of the furyl group for the hydroxyl group being greater than that exerted by the $CH_2COOC_2H_5$ group, or at least on a partial neutralization of the latter's influence by the furyl group in such a way that the production of the *syn*-oxime and, therefore, the formation of the isoxazolone, would be rendered more difficult than in the cases of acetacetic and benzoylacetic esters. Hantzsch[3] arranged various atomic groups in order of their attraction for the OH group of the oximes in the following way:

1. $—CH_2COOH$
2. $—CH_2.CH_2COOH$
3. $—COOH$
4. $—C_6H_5$
5. $—C_6H_4X$(*m* or *p*)
6. $—COC_6H_5$(*o*)
7. $—C_6H_4X$(*o*)
8. $—C_4H_3S$ (C_4H_3O)
9. $—C_nH_{2n-1}$
10. $—CH_3$

According to this arrangement the furyl group (8), coming after the phenyl group (4), should exert less attraction on the hydroxyl group than the former, and the oxime of furoylacetic ester should therefore be less stable than that of benzoylacetic ester. Since, as a matter of fact, the oxime of furoylacetic ester is much more stable than that of benzoyl-

[1] Ber. d. chem. Ges., **24**, 496.
[2] *Ibid.*, **24**, 1195.
[3] *Ibid.*, **25**, 2168.

acetic ester, the latter having never been prepared in the free[1] state, Hantzsch's views are inadequate to meet the situation.

Abegg[2] has studied the problem of the oximes from the standpoint of the dissociation theory and of electrostatics. He has shown that the stability of an oxime can be predicted from the difference in the electrostatic charges of the groups influencing the hydroxyl of the oxime. The intensity and nature of the charges can be determined from the influence of these groups on the dissociation constants of organic acids; the more negative a group the greater is the dissociation constant of the acid in which it is found. Thus he obtained the series: COOH, Cl, CH_2COOH, C_6H_5, H, and CH_3. That the CH_2COOH group is more negative than either the phenyl or the methyl groups can be seen from the following constants:

$(CH_2COOH)COOH$	$(C_6H_5)COOH$	$(CH_3)COOH$
Malonic acid.	Benzoic acid.	Acetic acid.
K 0.158	0.0060	0.00180

The more negative the radical, therefore, in the place of R, the more stable is the resulting oxime, since the attraction of the CH_2COOH group would be the more neutralized, and the less the likelihood of the isoxazolone formation. This theory of Abegg has been fully confirmed in this case. The dissociation constant of pyromucic acid is 0.707,[3] that is, more than ten times that of benzoic acid and nearly forty times that of acetic acid:

$(C_4H_3O)COOH$	$(C_6H_5)COOH$	$(CH_3)COOH$
Pyromucic acid.	Benzoic acid.	Acetic acid.
K 0.0707	0.0060	0.0018

One would therefore predict from these considerations that the oxime of furoylacetic ester would be considerably more stable than that of the benzoylacetic and acetacetic esters, and this is found to be the case. That the furyl group should be less positive than the phenyl or methyl group would

[1] Hantzsch: *Loc. cit.*, 2169.
[2] Ber. d. chem. Ges., **32**, 291.
[3] Ostwald: Z. physik. Chem., **3**, 385.

be expected from the fact that it contains oxygen, and, although is is not as negative as the CH_2COOH group, it can at any rate partially neutralize its influence on the hydroxyl group, and make the oxime of this ester fairly stable.

The action of semicarbazide on furoylacetic ester resembles that of hydroxylamine in that the product is decidedly more stable than that from the acetacetic ester.[1] The latter was found by Thiele and Stangen, who investigated the action of semicarbazide on acetacetic ester, to be so unstable that even warming in alcoholic solution changed it to a pyrazolone. We found it possible, on the other hand, to crystallize the semicarbazone of furoylacetic ester from alcohol without change, obtaining a substance of constant melting point, giving on analysis values agreeing with those for the semicarbazone.

Nitrous acid reacts with furoylacetic ester giving a derivative which, in light of the work of Victor Meyer[2] on the action of nitrous acid on acetacetic ester, is to be considered an isonitrosofuroylacetic ester. Like the isonitroso derivatives of acetacetic ester and benzoylacetic ester, it is a white substance dissolving in alkalies with a deep orange color but insoluble in acids.

Phenyl isocyanate reacts normally with the furoylacetic ester, forming a stable addition compound similar to those of acetacetic ester and related compounds, which, as has been shown by Michael[3] and by Dieckmann, Hoppe and Stein,[4] are the addition products of phenyl isocyanate on the $=CH_2$ group and not on the oxygen of the "enol" (C.OH) group, as one would expect from Goldschmidt and Meissler's results.[5]

The resulting product may act as a *keto* and *enol* compound, but as the compound obtained from furoylacetic ester is only difficultly soluble in alkalies, the keto form must predominate and pass to the *enol* only slowly. On the other hand, the

[1] Ann. Chem. (Liebig), **283**, 2.
[2] Ber. d. chem. Ges., **10**, 2077; **11**, 320; **21**, 1293.
[3] *Ibid.*, **16**, 2133.
[4] J. prakt. Chem., [2] **60**, 317. Ber. d. chem. Ges., **38**, 22. Ann. Chem. (Liebig), **363**, 64.
[5] Ber. d. chem. Ges., **37**, 4627.

presence of the *enol* form is indicated by the fact that with ferric chloride a purple color is obtained as with other related substances.

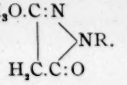
PART II. THE ACTION OF HYDRAZINES ON FUROYLACETIC ESTER. FURYLPYRAZOLONES.

The action of hydrazine on β-ketonic esters has been shown to take place in two stages. At first a hydrazone is formed by the splitting off of water and then, on heating this, alcohol is given off with the formation of a pyrazolone. In the case of acetacetic ester the hydrazone was isolated by Nef[1] and by Michael,[2] who obtained it in a pure state, while Fischer[3] and Knorr[4] had obtained it only in a very impure condition.

The first step in the reaction between the ester and the hydrazine, the separation of the water, is easily seen if no solvent is used, as the clear mixture becomes turbid on slight warming[5] or even on standing. The turbidity soon disappears on further warming, however, the water dissolving in the alcohol that splits off.

Although no intermediate product corresponding to the hydrazone of acetacetic ester[6] has been isolated in the case of furoylacetic ester, it is probable that the reaction takes place in two stages, as with phenylhydrazine. The separation of the water in the first stage causes a well-marked though transient turbidity. With hydrazine hydrate, however, this cannot be seen because of the presence of a solvent, and in the case of substituted phenylhydrazines the reaction had to be carried out at such a high temperature that the splitting off of water and alcohol were simultaneous.

When the free hydrazine or its salt, as in the case of the sodium phenylhydrazine-*p*-sulphonate, was used, a 5-pyrazolone was obtained,



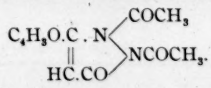
[1] Ann. Chem. (Liebig), **266**, 71.
[2] THIS JOURNAL, **14**, 518.
[3] Ber. d. chem. Ges., **16**, 661.
[4] *Ibid.*, **16**, 2597.
[5] Knorr and Klotz: *Ibid.*, **20**, 2546.
[6] Curtius and Jay: J. prakt. Chem., [2] **39**, 51.

Our reasons for assigning the carbonyl group to the 5-position are the facts that this reaction is entirely analogous to that of acetacetic ester, and that all our products gave a *red* isonitroso derivative which Michaelis has shown to be characteristic of 5-pyrazolones, while the 3-pyrazolones give *green* nitroso derivatives.[1] This point was confirmed by the preparation of 1-phenyl-5-furyl-3-pyrazolone, which gave a *green* nitroso compound with nitrous acid. In the case of the 3-furyl- and 1-phenyl-3-furylpyrazolones the action of benzaldehyde furnishes further evidence for the 5-position of the carbonyl group, since these pyrazolones react with one molecule of benzaldehyde forming red or brown compounds in which the $C_6H_5CH=$ group is united to only one molecule of the pyrazolone, a reaction impossible in the case of 3-pyrazolones which do not contain a methylene group.[2]

None of these pyrazolones gives the "pyrazole blue" reaction with ferric chloride. The colors given with that reagent vary from red to green, according to the substituting groups, but do not approach the beautiful blue given by the acetacetic ester derivatives. This behavior, however, is not unknown among pyrazolones; thus the 1-methyl-3-phenyl-5-pyrazolone gives a red color with ferric chloride, but no "pyrazole blue."[3]

Derivatives of 3-Furyl-5-pyrazolone.

3-Furyl-5-pyrazolone, prepared by the action of hydrazine sulphate on furoylacetic ester, gives with acetic anhydride a monacetyl derivative in which the acetyl group is undoubtedly on the 1-nitrogen, as this contains a free imide group. The formula assigned to this product is therefore that of 1-acetyl-3-furyl-5-pyrazolone. In the case of the action of acetyl chloride in pyridine solution a diacetyl derivative is obtained and the second acetyl group is probably attached to the second nitrogen as in the formula below:

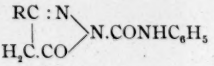


[1] H. Dorr: Diss., Rostock, 1906, p. 8. Michaelis: Ann Chem. (Liebig), **350**, 288.
[2] Knorr: Ber. d. chem. Ges., **20**, 2548. Lachowicz: Monats. Chem., **17**, 357. Stolz: Ber. d. chem. Ges., **28**, 631.
[3] Michaelis and Dorn: Ann. Chem. (Liebig), **353**, 164.

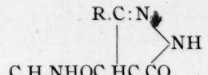
It is much more likely that the pyrazolone has acted in its imine rather than in its phenol form. So far no acetyl derivatives of the latter type have been prepared, the accepted formula for these compounds having the acetyl bound to nitrogen.[1] That both acetyl groups are bound either to nitrogen or to nitrogen and oxygen is shown by the fact that they can be saponified with alkalies, which would not take place if one or both were bound to carbon.[2]

The action of phenyl isocyanate has never before been tried on the pyrazolones. Michaelis and Lampe[3] effected a condensation with phenylpyrazolidine, obtaining a phenylurea which they looked upon as a semicarbazone.

Gebhardt[4] has shown that phenyl isocyanate reacts on the =NH group in secondary amines and Kuhn[5] that the reaction takes place with amides also, as, for instance, with acetanilide. With the pyrazolone the reaction may take place in two ways. The imino group NH may be the one to react or else the $CH_2.C:O$ group may be the active one, as Michael has shown it to be the case with acetacetic ester, and similar compounds, and phenyl isocyanate. In the pyrazolones we may have "enol" and "keto" compounds, as in acetacetic ester, but it would be unlikely that the isocyanate would react with the hydroxyl group, since Michaelis[6] has shown that in such cases the methylene group is the active one, and moreover, Leuckardt[7] found that in aminophenols the isocyanate goes to the nitrogen rather than to the hydroxyl group. There are therefore two possibilities for the condensation of phenyl isocyanate with the pyrazolones:



I.



II.

[1] von Rothenburg: J. prakt. Chem., [2] **50,** 228. Curtius: *Ibid.*, [2] **50,** 511.
[2] Nef: Ann Chem. (Liebig), **266,** 127.
[3] *Ibid.*, **274,** 327.
[4] Ber. d. chem. Ges., **17,** 2092.
[5] *Ibid.*, **17,** 2883.
[6] Ann. Chem. (Liebig), **363,** 64.
[7] J. prakt. Chem., [2] **41,** 301.

Of these, formula (I) is the more probable, since phenyl isocyanate shows a great tendency to form phenylureas. Moreover, its reaction with the CH_2CO group is a slow one unless catalyzed by alkalies; so that it is doubtful if it would take place in this case at all. That the imino group is active when attached to another nitrogen in a ring compound was shown by Michaelis and Lampe in condensing the isocyanate with a pyrazolidine.

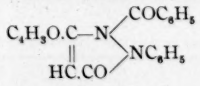
Benzaldehyde reacted with the 3-furylpyrazolone forming a light brown compound which, as analysis showed, contained only *one* molecule of pyrazolone condensed with one of aldehyde.

Diazobenzene chloride reacts on the CH_2 group of the 3-furyl-5-pyrazolone giving a brilliant red condensation product, a reaction which is characteristic of pyrazolones in general. The resulting compound may be regarded either as a hydrazone or a diazo compound, the latter being the more generally accepted view.

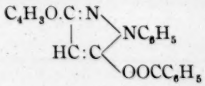
Derivatives of 1-Phenyl-3-furyl-5-pyrazolone.

1-Phenyl-3-furyl-5-pyrazolone is a very weak base and although it forms a hydrochloride, this, if dried too long, loses its hydrochloric acid and is also readily hydrolyzed by water. Knorr obtained from the 1-phenyl-3-methylpyrazolone a similarly unstable salt, which he supposed from his analyses crystallized with one molecule of water,[1] although he was unable to determine the water directly. Our hydrochloride also gave low results in the chlorine determination, but as we show in the experimental part, this is due to a partial loss of hydrochloric acid during the drying.

The Schotten-Baumann reaction gives a monobenzoyl derivative with 1-phenyl-3-furyl-5-pyrazolone, and as the benzoate thus obtained is readily saponified by alkalies, there are only two possible formulas for it:



I.



II.

[1] Ann. Chem. (Liebig), **238**, 152.

In view of Knorr's[1] work on similar compounds from 1-phenyl-3-methylpyrazolone, formula II seems to be the more likely one.

This pyrazolone reacts with acetyl chloride, giving a monacetyl derivative, which can be saponified by alkalies and which will therefore be considered a 1-phenyl-2-acetyl-3-furyl-5-pyrazolone.

With benzaldehyde the reaction is similar to that of the 3-furylpyrazolone, a red derivative being obtained in this case with one molecule of benzaldehyde.

With diazobenzene chloride a red 4-azobenzenepyrazolone results as in the case of the 3-furyl compound, and diazonaphthalene chloride acts in a similar way, one molecule of it condensing with one of the pyrazolone, hydrochloric acid being eliminated.

Nitrous acid acts in a normal manner on the CH_2 group of the phenylfuryl-5-pyrazolone, giving, like the phenylmethylpyrazolone, an isonitroso derivative.[2]

1-Phenyl-2-methyl-3-furyl-5-pyrazolone.—Methyl iodide reacts on the 1-phenyl-3-furylpyrazolone in a manner entirely similar to the action of the same reagent on the corresponding phenylmethylpyrazolone,[3] adding itself to the 2-nitrogen and forming the hydriodide of the base, the pyrazolone reacting in this case as an imino compound.

By treating this salt with sodic hydroxide the free base can be obtained, which, however, is so hygroscopic and passes so easily into unmanageable tarry compounds that it has not been studied in the free state. The salts, on the contrary, crystallize very well, are decidedly stable and through them all our knowledge of this furyl analogue of "antipyrine"[4] has been gained. The hydrochloride, for instance, may be readily formed by passing dry hydrochloric acid into a dry ethereal solution of the base.

That the CH_3 group enters in the 2-position was shown by the fact that symmetrical methylphenylhydrazine reacts on furoylacetic ester and from the reaction products it was

[1] Ber. d. chem. Ges., **30**, 928.
[2] Knorr: Ann. Chem. (Liebig), **238**, 185.
[3] Knorr: *Ibid.*, **238**, 203. Ber. d. chem. Ges., **17**, 2037.
[4] Knorr: *Ibid.*, **238**, 206.

possible to isolate the hydrochloride of 1-phenyl-2-methyl-3-furyl-5-pyrazolone identical with the one made from hydrochloric acid and the base set free from the methyl iodide addition product described above. Further evidence on this point was furnished by the decomposition of the nitroso-1-phenyl-2-methyl-3-furyl-5-pyrazolone with alkalies, symmetrical methylphenylhydrazine being obtained. From these two reactions the position of the methyl group is established; they are quite similar to those of antipyrine itself. Its salts are readily hydrolyzed by water with the formation of a brown insoluble oil, which, however, dissolves if the solution is made strongly acid. Towards ferric chloride, picric acid and platinic acid it behaves exactly like antipyrine.

Nitrous acid reacts on this body, giving a product similar to that obtained from antipyrine, which, as in the case of the 3-pyrazolones, is shown to be a true nitroso compound by its green color, but it is interesting to note that it gives a red hydrochloride which is hydrolyzed very readily to the green nitroso base. The introduction of the nitroso group in the antipyrine molecule decreases its stability and by the action of alkalies methylphenylhydrazine can be split off very easily, as mentioned above.

The pyrazolone formula has been assigned to this compound because the betain structure of the antipyrines is as yet unsettled and all the reactions of this body given here can be explained perfectly well by the original formula of Knorr.

The physiological properties of this base have not been determined as yet. The main difficulty in the way of studying them is its insolubility in water and the readiness with which its salts are hydrolyzed with the formation of an insoluble oil.

The pyrazolones included in this paper are, besides those obtained with hydrazine and phenylhydrazine, which have been studied in some detail, those made from *p*-bromphenylhydrazine, *m*-nitrophenylhydrazine and *p*-sulphonylphenylhydrazine. They are all considerably more acidic than the derivatives in which no substituting groups are present, and in their properties resemble closely the corresponding deriva-

tives from acetacetic ester except as to the "pyrazole blue" reaction. Thus the *p*-sulphonylphenylpyrazolone blackens, without melting, at 295°, in which respect it behaves like the 1-*p*-sulphonylphenyl-3-methylpyrazolone,[1] and like it it dissolves readily in alkalies but not in acids. The *p*-brom derivative forms white crystals, like the corresponding acetacetic ester derivative,[2] but melts at a lower temperature, the melting points being 160°–161° and 175°, respectively, while the 1-*m*-nitrophenyl compound resembles the acetacetic ester derivative in being colored yellow[3] and dissolving easily in alkalies but not in acids.

1-Phenyl-5-furyl-3-pyrazolone.—Following Mayer's[4] method for 3-pyrazolones, we attempted to obtain 1-phenyl-5-furyl-3-pyrazolone by the action of acetylphenylhydrazine and phosphorus trichloride on furoylacetic ester, but the yield did not rise above 0.1 per cent. and neither by changing the quantities of acetylphenylhydrazine nor by carrying on the reaction at varying temperatures could it be improved. Owing to scarcity of material, this work was not extended beyond the preparation of a sufficient amount of this pyrazolone for analysis and study of some of its reactions. It gave a *green* nitroso derivative with nitrous acid, while the 5-compound gave a red *isonitroso* compound, and besides this radical difference it is distinguished from its isomer by having an entirely different form of crystals, different solubilities and a slightly lower melting point. This last physical property is a remarkable one, as the 3-pyrazolones generally melt higher than the corresponding 5-compounds.[5]

The difficulty in preparing this pyrazolone, accepting Mayer's reaction as correct, may be due to the ester reacting mostly as a "*keto*" body, the "*enol*" compound being very slow to form. In that case the reaction would stop at the end of the first step and proceed but slowly. It may also be accounted for by the reaction of the phosphorus oxychloride on the

[1] Ber. d. chem. Ges., **25**, 1942.
[2] *Ibid.*, **33**, 2007.
[3] *Ibid.*, **33**, 2598.
[4] *Ibid.*, **36**, 717.
[5] Stolz: *Ibid.*, **38**, 3275.

furyl group giving resinous tarry products, as in the case of 1-phenyl-3-furyl-5-pyrazolone.[1]

EXPERIMENTAL.

Materials Used.—The starting material for this research was a sample of furfural which had been specially distilled for the late Professor H. B. Hill by Dr. R. Squibb, of New York. As it had stood for several years before this work was begun, it was found necessary to redistil it in order to remove polymers and decomposition products formed on standing. The fraction collected boiled between 155°–165° and constituted about two-thirds of the sample. It had a light amber color, gave the usual furfural reactions, and was not allowed to stand more than a few hours before being oxidized to pyromucic acid.

On account of the large quantities of starting material needed in this research the pyromucic acid was made by the method of Ulrich[2] as modified in this laboratory. This consisted in treating the furfural with a concentrated sodium hydroxide solution.

Although one-half of the furfural was lost as furfuryl alcohol which could not be recovered from the reaction products, this method had the advantage that large quantities could be handled in one operation. About two liters of furfural were treated in this manner each time, and from them 800–900 grams of fairly pure pyromucic acid, which had a light buff color and melted at 130°, were obtained.

The method of Volhard,[3] in which potassium permanganate is used to oxidize furfural to pyromucic acid, was tried but found too tedious for handling the large quantities needed for this work and besides did not yield directly a very pure product. The methods of Frankland and Aston[4] and of Freundler,[5] both modifications of Volhard's method, were also tried but found unsatisfactory for our purposes.

Ethyl pyromucate was obtained from this acid by dissolving it in about three to four times its weight of absolute alco-

[1] See Experimental Part.
[2] Jahres. d. Chem., **1860**, 267.
[3] Ann. Chem. (Liebig), **261**, 379.
[4] Chem. Centralb., **1901**, II, 985.
[5] Bull. soc. chim., **17**, 609.

hol and passing dry hydrochloric acid gas into the solution until its weight had increased by ten per cent. of that of the alcohol. The mixture was then heated in a flask attached to a reflux condenser for three or four hours, the alcohol distilled off and the residue poured into cold water, when a dark oil separated out, which, on scratching, crystallized to a mass of brown crystals. These were filtered off, dried by exposure to the air and distilled under reduced pressure, the first fraction and the residue being rejected. Thus purified, the ester consisted of long transparent prisms melting at 34°. The ethyl acetate used was obtained from Schuchardt and was thoroughly dried over calcium chloride and redistilled before using.

Furoylacetic Ester.—The method given by Bouveault and followed closely by Sandelin for the synthesis of furoylacetic ester consists in treating one mole of ethyl pyromucate with two moles of ethyl acetate in the presence of one atom of sodium. At the beginning of this research that method was closely followed but the poor yields obtained made it necessary to look for a more economical one. It was soon found that the best yields, 30–40 per cent. of the calculated, were obtained by using small amounts of material at a time, not more than 15 grams of ethyl pyromucate with the corresponding quantities of sodium and ethyl acetate. Whenever larger quantities than these were used, the yields were considerably lowered. The action of sodium in the form of wire was then tried and found to be much more effective and convenient, and it was also found that increasing the proportion of sodium and ethyl acetate improved the yield. With these two improvements as large a quantity of ethyl pyromucate as was available could be handled in one operation and the yield of furoylacetic ester was raised to 48 per cent. of the theoretical or to 70 per cent. of the ethyl pyromucate used.

The following proportions gave the best results: One mole of ethyl pyromucate was dissolved in 3.5 moles of ethyl acetate and into the mixture two and a half atomic weights of sodium were squeezed through a sodium press. The reaction, if the materials are throughly dry, begins slowly, and to start it it is generally necessary to heat on the steam bath under a

reflux condenser for about half an hour. As soon as it begins, however, it proceeds violently and the flask must be cooled by pouring water over it, else some ethyl acetate will be forced out of the top of the condenser; for this reason it is preferable to employ a copper flask and thus avoid danger of breakage on cooling. After about ten minutes the reaction becomes less violent and the solution of the sodium proceeds gently, the mixture growing dark in color. At the end of one hour a half mole of dry ethyl acetate is added to prevent the reaction mixture from caking and the heating continued for two hours longer, 3 hours in all. When all the sodium is dissolved, the reaction mixture is poured into a dish and acidified with dilute hydrochloric acid. This causes the separation of a dark brown oil which is extracted with two or three times its volume of ether and dried thoroughly over calcium chloride. The ether is then evaporated off and the residue fractionated under 20 mm. pressure. The fraction that boils below 100° consists mainly of ethyl acetate and acetacetic ester. The thermometer then rises gradually up to 160°, very little liquid distilling over, but finally when the temperature reaches 170° a light yellow oil begins to appear rapidly. The receiver is then changed and the ester, which distills over entirely within 3°, is collected. If the ethyl pyromucate has not been thoroughly purified by distillation, pyromucic acid appears at this point in the form of white needles solidifying in the condenser tube.

Furoylacetic ester thus prepared is a light yellow, heavy oil of a faint pleasant odor, miscible with alcohol and ether in all proportions but insoluble in water. When pure it is decidedly stable, darkening only on long standing. The boiling points as given by Bouveault, 143°–145° (10 mm.), and by Sandelin, 170° (20 mm.), have been verified. The ester solidifies in a mixture of solid carbon dioxide and alcohol to a mass of white crystals, and if it is allowed to cool slowly these appear as long silky needles radiating from a nucleus. With ferric chloride it gives a wine-red color and reduces ammoniacal silver oxide, depositing a mirror. The ester forms

well-defined salts, but does not remain dissolved in sodic or potassic hydroxides because the salts formed are nearly insoluble in water. In ammonia it dissolves readily.

The specific gravity was found to be 1.165 at 17°.

The Action of Potassium Hydroxide.—On boiling some of the ester with concentrated potassium hydroxide for some time a dark brown liquid was obtained which was acidified and extracted with ether. The extract, after thorough drying over calcium chloride, was evaporated, when dark brown needles were deposited. These were decolorized with bone black, crystallized from hot water, dried and sublimed. Thus purified they were obtained in the form of long white silky needles melting at 129°–130°, possessing the characteristic odor of pyromucic acid and giving a yellow precipitate with ferric chloride. Their solution in warm water was acid towards litmus and set free carbon dioxide from a sodium carbonate solution. These reactions show that the needles are pyromucic acid.

Salts of Furoylacetic Ester.

Sodium Salt, $C_9H_9O_4Na$.—To 4 grams of the ester dissolved in 5 cc. of alcohol were added 8 grams of sodium hydroxide dissolved in 10 cc. of water, the reaction being carried out at 0° to avoid saponification. The solution very soon became pasty from the separation of white needles of the sodium salt, which were filtered off, washed with alcohol and crystallized from hot alcohol.

Analysis:

0.2500 gram of the salt, dried over concentrated sulphuric acid *in vacuo*, gave 0.0887 gram Na_2SO_4.

	Calculated for $C_9H_9O_4Na$.	Found.
Na	11.27	11.50

Potassium Salt.—When a dilute potassium hydroxide solution was used instead of sodium hydroxide, long, white, silky needles separated out, unquestionably the potassium salt, although they were not analyzed.

Copper Salt, $(C_4H_3OCOCHCOOC_2H_5)_2Cu$.—This salt was prepared according to Sandelin's directions by treating an alcohol solution of the ester with a water solution of copper acetate. The salt precipitated out of the solution in the form of small green needles, which were filtered off and dried.

Analysis:

0.5976 gram of the salt, dried *in vacuo*, gave on ignition 0.1084 gram of CuO.

	Calculated for $(C_9H_9O_4)_2Cu$.	Found.
Cu	14.82	14.84

The copper salt crystallizes in small green needles soluble in benzene and hot alcohol but insoluble in ether. On heating it with alcohol for some time and allowing the solution to stand, thick blue plates separate out.

The Action of Hydroxylamine.

Oxime of Furoylacetic Ester, $C_4H_3O.C(NOH).CH_2COOC_2H_5$.—This substance was obtained by allowing one molecule of hydroxylamine hydrochloride, treated with the corresponding amount of sodium acetate, to act on one molecule of the ester, in a dilute alcoholic solution. After allowing the mixture to stand for about three hours, a mass of long white crystals separated which were filtered with suction and recrystallized from dilute alcohol. After three crystallizations the constant melting point, 131°–132°, was reached.

Analysis: The substance was dried over concentrated sulphuric acid *in vacuo*.

I. 0.2163 gram gave 0.4372 gram CO_2 and 0.1058 gram H_2O.

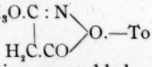
II. 0.3995 gram of the substance gave 28.80 cc. of N at 20°.0 and 753 mm.

III. 0.1887 gram of the substance gave 12.6 cc. of N at 15°.2 and 760 mm.

IV. 0.4008 gram of the substance gave 26.70 cc. of N at 23° and 747 mm.

	Calculated for $C_9H_{11}O_4N$.	Found. I.	II.	III.	IV.
C	54.82	55.13	....	....	....
H	5.58	5.48	....	....	....
N	7.11	....	8.15	7.86	7.34

Thus crystallized the oxime consists of long silky needles soluble in ether, alcohol or hot benzene, but insoluble in water or ligroin. It is soluble in alkalies and in concentrated acids.

3-*Furylisoxazolone*,  .—To 10 grams of the ester in dilute alcohol solution were added 5 grams of hydroxylamine hydrochloride and enough potassium hydroxide to make the solution strongly alkaline. The mixture was warmed for some time on the steam bath, cooled and acidified with hydrochloric acid, when a voluminous precipitate of white needles separated out. This was filtered off, washed and crystallized from dilute alcohol until it had a constant melting point.

Analysis: The substance was dried *in vacuo*.

I. 0.2194 gram gave 0.4474 gram CO_2 and 0.0745 gram H_2O.

II. 0.3238 gram gave 26.55 cc. of N at 759 mm. and 23°.0.

	Calculated for $C_7H_5O_3N$.	Found. I.	II.
C	35.63	55.61	....
H	3.33	3.77	....
N	9.27	....	9.22

This isoxazolone crystallizes from dilute alcohol in long flat needles, which are colored very slightly brown if in making the compound the heating is prolonged, but if this be brief the needles can be obtained perfectly white in color. When dipped into the bath at 145°, the melting point of the substance is 148°–149°, but if allowed to warm with the bath, the melting point is 147°–148°. In both cases the substance decomposes on melting. This compound is soluble in water or benzene when hot, slightly so in hot ligroin, but essentially insoluble in these three solvents when cold; soluble in cold

acetone and insoluble in ether. Alkalies dissolve it readily and acids reprecipitate it unchanged. It is insoluble in concentrated hydrochloric acid.

The Action of Semicarbazide.

Semicarbazone of Furoylacetic Ester, $C_4H_3O.C(:NNHCONH_2).CH_2COOC_2H_5$

This compound was formed by heating one mole of the ester, in dilute alcohol solution, with one mole of semicarbazide hydrochloride and the corresponding amount of sodium acetate. After standing for a few hours white crystals separated out. These were filtered off, washed with water and recrystallized from absolute alcohol until the melting point became constant.

Analysis: The substance was dried *in vacuo*.

I. 0.1953 gram gave 30.95 cc. of N at 27°.5 and 757 mm.

II. 0.2502 gram gave 41.38 cc. of N at 22°.5 and 747 mm.

	Calculated for $C_{10}H_{13}O_4N_3$.	Found. I.	II.
N	17.57	17.55	18.37

The semicarbazone crystallizes in small, flat, rhombic plates which decompose slightly on melting. They are soluble in hot absolute alcohol, hot benzene and hot chloroform, but insoluble in hot or cold ligroin.

The Action of Nitrous Acid.

Isonitrosofuroylacetic Ester, $C_4H_3OCOC(:NOH)COOC_2H_5$.—To 5 grams of furoylacetic ester in dilute acetic acid were added slowly 4 grams of sodium nitrite. On allowing the solution to stand for about two hours an abundant white, flocculent precipitate separated out. This was filtered off and crystallized from hot water, whence it was obtained in the form of small white needles having the constant melting point 128°–129°.

Analysis: The substance was dried *in vacuo*.

I. 0.2317 gram gave 0.4394 gram CO_2 and 0.0955 gram H_2O.

II. 0.3035 gram gave 18.62 cc. of N at 25°.1 and 773 mm.

	Calculated for $C_9H_9O_5N$.	Found. I.	II.
C	51.19	51.72	....
H	4.26	4.59	....
N	6.63	....	6.96

The isonitrosofuroylacetic ester is soluble in alcohol, ether, benzene, and hot water. Alkalies dissolve it readily, giving an orange solution from which the white nitroso derivative is reprecipitated on acidifying.

The Action of Phenyl Isocyanate.

Anilide of Furoylmalonic Ester, $C_4H_3OCOCHCONHC_6H_5$.—
$\quad\quad\quad

point, the substance is allowed to warm up with the bath it begins to soften at about 138° and melts completely at 146°. When dipped in the bath at 143° and warmed up slowly the melting point is 148°–150°, but it does not melt at 144° when held at that temperature for some time.

3-Furylpyrazolone, $C_4H_3O.C{:}N$ / $H_2C.C$ $\rangle$ NH.—This compound was made by heating a dilute alcohol solution of furoylacetic ester with hydrazine sulphate and sodium acetate in molecular proportions. It can also be obtained by heating the ester with a solution of hydrazine hydrate, neutralizing with acetic acid and salting out with sodium acetate. The pyrazolone separates out as a brown crystalline powder, which can be obtained perfectly white by washing with ether and crystallizing from dilute methyl alcohol.

Analysis: The substance was dried *in vacuo*.

I. 0.2073 gram of the substance gave 0.4290 gram CO_2 and 0.0813 gram H_2O.

II. 0.1652 gram of the substance gave 27.22 cc. of N at 22°.4 and 756 mm.

	Calculated for $C_7H_6O_2N_2$.	Found. I.	Found. II.
C	56.00	56.44	....
H	4.00	4.41	....
N	18.66	....	18.47

The pyrazolone crystallizes in small rectangular plates which begin to decompose at about 200°, finally blackening completely and melting at 223°. It is soluble in methyl or ethyl alcohol or warm glacial acetic acid, and slightly soluble in water or ether. Alkalies and acids dissolve it readily. In an alcoholic solution diluted with water it reacts acid towards litmus. With nitrous acid (sodium nitrite and hydrochloric acid) it gives a deep red solution from which no precipitate can be obtained either by neutralizing or making alkaline. It gives precipitates with chlorauric or chloroplatinic acids and a white flocculent precipitate with silver nitrate. It does not give the "pyrazole blue" reaction.

Picrate, $C_7H_6N_2O_2.C_6H_2(NO_2)_3OH$.—The picrate was obtained as a light yellow precipitate by adding an alcoholic solution of the pyrazolone to a saturated aqueous solution of picric acid. The precipitate was filtered off and crystallized from a mixture of alcohol and benzene.

Analysis: The substance was dried *in vacuo*.

0.1191 gram gave 19.72 cc. of N at 21° and 767 mm.

	Calculated for $C_{13}H_9O_9N_5$.	Found.
N	18.47	18.98

The picrate crystallizes in small prisms with rounded ends, decomposing completely at 192°, although the change begins considerably below 190°. It is soluble in alcohol, slightly soluble in hot benzene, or hot water, but insoluble in ether.

1-Acetyl-3-furyl-5-pyrazolone, $C_4H_3O.C:N$ / $H_2C.CO$ \ $N.COCH_3$.—On warming the pyrazolone with a slight excess of acetic anhydride and pouring the reaction product into cold water, an oil separates out which, after a while, crystallizes to a mass of small radiating needles. These were filtered off, dried, and crystallized until they showed a constant melting point.

Analysis:

0.1522 gram of the substance dried *in vacuo* gave 20.61 cc. N at 27° and 759 mm.

	Calculated for $C_9H_8O_3N_2$.	Found.
N	14.59	14.93

This substance crystallizes in long white needles melting at 153°–154° to a viscous liquid. It is soluble in alcohol, hot benzene or hot ligroin, but insoluble in ether or in water.

On boiling with dilute sodium hydroxide to complete solution the acetyl group is split off and on neutralizing with acetic acid the pyrazolone is obtained as a precipitate of minute rectangular plates melting at 220°.

1,2-Diacetyl-3-furyl-5-pyrazolone, $C_4H_3O.C.N(COCH_3)$ / $HC.CO$ \ $N.COCH_3$.—

This compound was obtained by adding acetyl chloride to a pyridine solution of the pyrazolone and pouring the reaction mixture into cold water. The oil that separated out soon solidified and the dried product was crystallized from ligroin until its melting point was constant.

Analysis:

0.1689 gram of the substance, dried *in vacuo*, gave 18.78 cc. N at 26°.5 and 757 mm.

	Calculated for $C_{11}H_{10}O_4N_2$.	Found.
N	11.96	12.26

This diacetyl derivative crystallizes in long white silky needles melting at 102°, and soluble in ether, alcohol or benzene, but insoluble in water. On boiling with dilute sodium hydroxide to complete solution both acetyl groups are saponified and 3-furyl-5-pyrazolone is obtained, crystallizing in small rectangular plates and melting at 220°.

Furylpyrazolonephenylurea, $C_4H_3O.C:N$ / $H_3C.CO$ \> $NCONHC_6H_5$.—

This compound was prepared by the action of phenyl isocyanate on the pyrazolone suspended in benzene. After washing off the excess of phenyl isocyanate, it was crystallized from 90 per cent. alcohol until the melting point became constant.

Analysis:

0.1350 gram of the substance, dried *in vacuo*, gave 18.65 cc. N at 27° and 765 mm.

	Calculated for $C_{14}H_{11}O_3N_3$.	Found.
N	15.62	15.33

This compound melts at 192° and is soluble in hot chloroform, alcohol or benzene, but insoluble in water or ligroin.

4-Benzylidine-3-furyl-5-pyrazolone, $C_4H_3O.C:N$ / $C_6H_5CH:C.CO$ \> $NH.$ — A

glacial acetic acid solution of the pyrazolone was heated with an excess of benzaldehyde for about fifteen minutes on the steam bath. The solution thickened with the separation of a

brown precipitate which, after thorough washing, yielded a light brown powder. As this could not be crystallized, it was repeatedly washed with ether and alcohol to remove any unconverted pyrazolone and benzaldehyde, dried and analyzed.

Analysis:

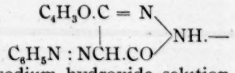
0.2081 gram of the substance dried *in vacuo* gave 20.52 cc. N at 18°.5 and 766 mm. pressure.

	Calculated for $C_{14}H_{10}O_2N_2$.	Found.
N	11.75	11.47

This compound is insoluble in most organic solvents. When heated with nitrobenzene or acetophenone, some goes into solution, but on cooling only a very small amount separates out. It does not melt at 300°. Heated with sodium hydroxide solution, it gives off an odor of benzaldehyde. Concentrated sulphuric acid dissolves it, giving a red solution.

On heating the pyrazolone in a similar manner with salicylic aldehyde instead of benzaldehyde a substance was obtained, infusible at 260°, soluble in ligroin, alcohol, alkalies and acids, but insoluble in ether or in water. This is probably an analogous condensation product with salicylic aldehyde, but it was not analyzed.

3-Furyl-4-azobenzene-5-pyrazolone,



To 2 grams of the pyrazolone in sodium hydroxide solution were added 0.8 gram of aniline carefully diazotized with the required amount of sodium nitrite and hydrochloric acid. A red precipitate separated at once which was filtered off and crystallized from alcohol until it had a constant melting point.

Analysis:

0.1197 gram of the substance dried *in vacuo* gave 24.10 cc. N at 25°.6 and 752 mm.

	Calculated for $C_{13}H_{10}O_2N_4$.	Found.
N	22.05	22.15

This azo derivative crystallizes from alcohol in beautiful

red, transparent prisms, melting at 182°–183° to a thick viscous liquid adhering to the sides of the melting-point tube. It is slightly soluble in alcohol, ether or benzene, in the cold, and readily in the warm solvent.

1-Phenyl-3-furyl-5-pyrazolone, $C_4H_3OC:N$ / $H_2C.CO$ > NC_6H_5. — This compound was prepared by allowing one molecule of phenylhydrazine to react on one molecule of furoylacetic ester at the temperature of the steam bath, according to the method of Sandelin.[1] Very soon after the warming is begun the mixture becomes turbid, probably from the separation of water; this turbidity disappears rapidly, however, and after 10 or 15 minutes' heating the mass solidifies from the separation of pyrazolone, which can be obtained pure by washing with ether and crystallizing from hot absolute alcohol. Thus purified, the pyrazolone consists of small leaflets appearing under the microscope as minute rhombic plates. The melting point as given by Sandelin, 179°, was found to be correct. 1-Phenyl-3-furyl-5-pyrazolone is readily soluble in alkalies or strong acids. With ammonia, on standing, it gives a purplish red solution and with chlorplatinic or chlorauric acid, brown precipitates. It does not combine with picric acid, neither does it give the "pyrazole blue" reaction. If boiled with ferric chloride in alcohol solution a deep red color is obtained, and on pouring this into water a gray precipitate separates which dissolves in chloroform with a deep red color. Aqueous ferric chloride solution, even when concentrated, is without action on this pyrazolone.

Hydrochloride, $C_{13}H_{10}O_2N_2HCl$.—Into a suspension of the pyrazolone in absolute alcohol dry hydrochloric acid gas was passed until all the pyrazolone was dissolved. The solution was then poured into a large excess of ether which caused the separation of a colorless oil, solidifying on scratching to a mass of white crystals. These were filtered off, thoroughly washed with ether and crystallized from a mixture of alcohol and ethyl acetate or of alcohol and benzene. The per-

[1] Ber. d. chem. Ges., **33**, 492.

fectly white crystals were dried over concentrated sulphuric acid, then over caustic potash. Unless the drying was brief, decomposition quickly set in, the color changing to brown. In the first two analyses the drying was carried on *in vacuo* for a long time, in the third it lasted only four hours and the air was not exhausted.

Analysis:

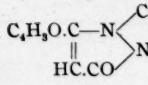
I. 0.2441 gram gave 0.1213 gram AgCl.
II. 0.2443 gram gave 0.1198 gram AgCl.
III. 0.2840 gram gave 0.1440 gram AgCl.

	Calculated for $C_{13}H_{11}O_2N_2Cl$.	Found. I.	II.	III.
Cl	13.52	12.29	12.12	12.54

The hydrochloride crystallizes in small white needles, soluble in alcohol or hot ethyl acetate, but insoluble in ether, benzene, or ligroin. Water hydrolyzes it, forming the pyrazolone. It is soluble in concentrated hydrochloric acid and melts at 122°–123° with decomposition.

Although the results of these analyses are a per cent. or more below the calculated values they leave no doubt as to the composition of the substance. The low percentage of chlorine was probably due to a loss of hydrochloric acid during the drying, for, as was already stated, there was a visible decomposition unless the drying was very brief, and the longer the drying the less was the amount of chlorine obtained. The only other probable hypothesis is that the salt contained half a molecule of alcohol, which would give 12.40 per cent. for chlorine, but in this case the specimen dried for 4 hours would have contained less chlorine than those dried for a longer time, whereas in fact just the reverse was the case. We feel, therefore, that this second hypothesis should be rejected, even although Knorr, from chlorine determinations only, thought the hydrochloride of his 1-phenyl-3-methylpyrazolone contained one molecule of water.

1-Phenyl-2-acetyl-3-furyl-5-pyrazolone



$C_4H_3O.C(=HC.CO)-N(COCH_3)NC_6H_5$.—This compound was readily obtained

by dissolving the pyrazolone in boiling acetic anhydride and pouring the solution into water, when an oil separated out, which, on scratching, crystallized to a yellowish white mass. This was filtered off and recrystallized from ligroin until it had a constant melting point.

Analysis:

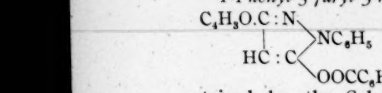
0.4196 gram of the substance dried *in vacuo* gave 39.81 cc. N at 25° and 756 mm.

	Calculated for $C_{18}H_{12}O_2N_2$.	Found.
N	10.44	10.52

The melting point of this compound is not very sharp, lying between 69°–72°. Under the microscope the crystals appear as flat, transparent prisms, slightly yellow in color. They are soluble in alcohol or benzene without difficulty, but insoluble in cold ligroin.

By boiling with alcoholic potash the acetyl group is split off and on acidifying with acetic acid the pyrazolone is precipitated out in the form of flat rhombic plates melting at 178°.

1-Phenyl-3-furyl-5-hydroxypyrazole Benzoate,



.—This benzoyl derivative was obtained by the Schotten-Baumann reaction, by dissolving the pyrazolone in sodium hydroxide and adding an excess of benzoyl chloride. After some time a yellowish mass of crystals separated out, which were finally filtered off, washed and crystallized until the melting point was constant.

Analysis:

0.2084 gram of the substance dried over concentrated sulphuric acid gave 15.81 cc. N at 21° and 763 mm.

	Calculated for $C_{20}H_{14}O_3N_2$.	Found.
N	8.48	8.69

This compound crystallizes from dilute alcohol in white needles melting at 113°–114° and dissolving easily in alcohol, ether, benzene or hot ligroin.

By boiling with alcoholic potash, the benzoyl group can be split off and on evaporating to dryness, acidifying and crystallizing from alcohol, the pyrazolone is obtained in the form of small rhombic plates melting at 177°.

1-Phenyl-3-furyl-4-isonitroso-5-pyrazolone,

$C_4H_3O.C:N$
$\quad\quad\quad

heating benzaldehyde with the pyrazolone in molecular proportions in an oil bath to 150°. The reaction began at about 120°, the color of the mixture becoming deep red and ebullition beginning; to complete it the temperature was raised to 150° and kept there until no more bubbles were given off, after which the reaction product was allowed to cool and dissolved in hot toluene, when, on cooling, the benzylidene derivative separated in the form of red flakes, showing no trace whatever of crystallization.

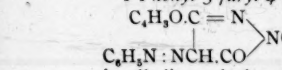
Analysis:

0.2112 gram of the substance dried *in vacuo* gave 15.85 cc. N at 22° and 763 mm.

	Calculated for $C_{20}H_{14}O_2N_2$.	Found.
N	8.91	8.53

The benzylidinepyrazolone is a reddish amorphous powder, insoluble in alcohol, ether, or benzene, readily soluble in hot toluene or in chloroform. Alkalies dissolve it with a pinkish color and on warming decompose it, giving off an odor of benzaldehyde. It is insoluble in hydrochloric acid, but in concentrated sulphuric acid it dissolves readily, forming a bright red solution. It decomposes at 210°–212°.

1-Phenyl-3-furyl-4-azobenzene-5-pyrazolone,



—To 2 grams of the pyrazolone in alkaline solution were added 0.8 gram of aniline, carefully diazotized with the required amount of sodium nitrite and hydrochloric acid. A brownish red paste separated from the solution at once and this was purified by repeated crystallizations from alcohol-benzene mixtures until the melting point was constant.

Analysis:

0.1539 gram of the substance gave 23.61 cc. N at 21°.8 and 754 mm.

	Calculated for $C_{18}H_{14}O_2N_4$.	Found.
N	16.97	17.36

This azobenzene pyrazolone crystallizes in long, light red,

slender needles, with smaller crystals adhering to and growing from them. It melts at 165° to a thick liquid adhering to the sides of the melting-point tube in a way similar to that of the 3-furyl-4-azobenzenepyrazolone, and decomposes at 205°. It is readily soluble in benzene or ethyl acetate, slightly soluble in ether, ligroin, or alcohol, and insoluble in water.

1-Phenyl-3-furyl-4-β-azonaphthalene-5-pyrazolone,

$$\begin{matrix} C_4H_3O.C = N \\ | \qquad\quad \diagdown \\ C_{10}H_7N : NCH.CO \end{matrix} \diagup NC_6H_5,$$

—To 2 grams of the pyrazolone in alkaline solution was added a solution of 1.3 grams of β-aminonaphthalene diazotized with hydrochloric acid and sodium nitrite until a drop of the solution gave a blue color with starch potassium iodide paper. A heavy, rusty-brown precipitate separated at once, which was filtered off and crystallized from a mixture of alcohol and benzene until it had a constant melting point.

Analysis:

0.1549 gram of the substance, dried *in vacuo*, gave 20.18 cc. N at 24°.5 and 749 mm.

	Calculated for $C_{23}H_{15}O_2N_4$.	Found.
N	14.74	14.35

This compound crystallizes in small, deep red needles, melting at 202°–203° to a thick viscous liquid, adhering to the sides of the melting-point tube. It it soluble in hot benzene, slightly soluble in the cold solvent, as well as in ether or alcohol, but insoluble in water or ligroin.

The action of diazotized substituted anilines was also tried, but the compounds were not analyzed. Diazotized sulphanilic acid added to a solution of the pyrazolone in dilute sodium hydroxide gave an amorphous red precipitate, soluble in alcohol, glacial acetic acid or hot water, but insoluble in benzene or ligroin. From none of these solvents could a crystallized product be obtained. Diazotized *p*-nitraniline gave a deep red precipitate under the same conditions. This was insoluble in water, but soluble in alcohol. From a hot dilute alcohol solution it could be obtained as an amorphous red powder. *p*-Toluidine gave a brown amorphous product.

Several experiments were undertaken to obtain the furyl-chlorpyrazole by treating the pyrazolone with phosphorus oxychloride according to the method of Michaelis.[1] In the cold or at the temperature of the steam bath the phosphorus oxychloride is without action. Heated in a sealed tube to 150°, the mixture of oxychloride and pyrazolone gave a charred resinous mass from which no definite product could be obtained.

1-Phenyl-2-methyl-3-furyl-5-pyrazolone.—Attempts to obtain the free base in a pure condition were unsuccessful owing to the ease with which it deliquesces and afterward passes into a tarry mass which does not solidify even over phosphorus pentoxide *in vacuo*. The best that could be done was to separate it in the form of a light brown amorphous powder by adding ligroin to its solution in chloroform, prepared by decomposing a salt of the base with sodium hydroxide and extracting with chloroform the brown oil that separated. The extract was then dried over calcium chloride and to it an excess of dry ligroin was added, when the base was precipitated as a light brown mass of curds which, by quickly transferring to a piece of biscuit ware and placing in a desiccator with phosphorus pentoxide, was obtained in the form of a light brown powder. If exposed to the air for a few minutes, moisture was quickly absorbed and the powder became a light brown tar that could not be dried in a desiccator. If the chloroform solution was evaporated *in vacuo* over concentrated sulphuric acid a varnishlike residue was left behind. The solvents used in this precipitation should be absolutely dry. No satisfactory analysis of this substance was made. This was not necessary as its identity was established by the analysis of its salts, which crystallize readily.

Hydriodide, $C_{14}H_{12}O_2N_2HI$.—This substance, which formed the starting material for further work on the 1-phenyl-2-methyl-3-furyl-5-pyrazolone, was readily obtained by heating equal weights of the pyrazolone and methyl iodide together with a little methyl alcohol in a sealed tube to 90°–100° for about 2 hours. On opening the tube the dark red liquid

[1] Ber. d. chem. Ges., **31**, 2907; **32**, 2402.

formed in the reaction crystallized in long, flat, almost colorless needles which were dissolved in alcohol and the last traces of color removed by passing sulphur dioxide into the solution. A large volume of ether was then added and the precipitated hydriodide crystallized from a benzene-alcohol mixture.

The substance was dried *in vacuo* and analyzed:

I. 0.2045 gram of the substance gave 0.1283 gram of AgI.

II. 0.1968 gram of the substance gave 14.59 cc. N at 29°.0 and 766 mm.

	Calculated for $C_{14}H_{12}O_2N_2HI$.	Found. I.	II.
I	34.51	33.90	....
N	7.61	...	8.15

These results are as near as could be expected when the slight stability of the compound is considered.

The hydriodide crystallizes in long, flat, transparent needles, which are very unstable, turning rapidly to yellowish green and then to brown. It is very soluble in methyl or ethyl alcohols or hot chloroform, but insoluble in ether, toluene, benzene, or ligroin. When moistened with water, the crystals form oily drops. It crystallizes from acetonitrile in tufts of needles. When pure it melts at 192°–193° with decomposition.

Hydrochloride, $C_{14}H_{12}O_2N_2HCl$.—On decomposing the iodide with strong sodium hydroxide the free base was obtained in the form of a light brown oil, which was extracted with chloroform and the solution thus obtained dried carefully over calcium chloride and saturated with a dry hydrochloric acid gas. After a short time the solution became almost solid, the hydrochloride separating in the form of light brown needles, which were filtered off, washed with ether and crystallized from a benzene-alcohol mixture. Repeated crystallizations did not completely remove the brown color. The substance was dried for analysis *in vacuo*.[1]

I. 0.2469 gram of the substance gave 0.1283 gram AgCl.

II. 0.2032 gram of the substance gave 17.75 cc. N at 20°.5 and 766 mm.

[1] Seven combustions for carbon and hydrogen were made with this substance, but no consistent results could be obtained even by using a very long combustion tube filled with lead chromate and containing two reduced copper spirals and a long silver coil.

	Calculated for $C_{14}H_{12}O_2N_2HCl$.	Found. I.	II.	III.
Cl	12.84	12.85	...	....
N	10.13	...	10.04	....

The hydrochloride crystallizes in light, buff-colored prisms perfectly transparent when seen under the microscope. It is much more stable than the iodide and melts with decomposition at 197°–198°. It is readily soluble in methyl or ethyl alcohol or hot chloroform, but insoluble in ether, benzene, or ligroin. Water hydrolyzes this substanec to an oil in the same way that it does the iodide. With ferric chloride it gives a deep red color and with chlorplatinic acid a light orange, crystalline precipitate. With picric acid a yellow picrate is obtained and with nitrous acid a beautifully crystallizing green nitroso derivative changing to red in acid solutions.

Hydrobromide, $C_{14}H_{12}O_2N_2HBr$.—If instead of passing hydrochloric acid into the chloroform solution of the base, dry hydrobromic acid was used, the hydrobromide of the base was obtained in the form of small white crystals, which were crystallized from chloroform until the melting point was constant. The substance was dried for analysis for two hours at 90°, then over phosphorus pentoxide *in vacuo*.

0.1795 gram of the substance gave 0.1040 gram AgBr.

	Calculated for $C_{14}H_{12}O_2N_2HBr$.	Found.
Br	24.92	24.65

The hydrobromide crystallizes from alcohol-benzene mixtures in small rectangular plates, soluble in alcohol or hot chloroform, but insoluble in ether, benzene or water. It melts with decomposition at 194°.

Picrate, $C_{14}H_{12}O_2N_2 . HOC_6H_2(NO_2)_3$.—On adding a solution of picric acid to an alcohol solution of the base a precipitate of yellow needles separated which was filtered off and crystallized from alcohol. The substance was dried for analysis *in vacuo*.

0.2035 gram of the substance gave 25.76 cc. N at 11°.2 and 750 mm. pressure.

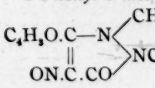
	Calculated for $C_{20}H_{18}O_6N_2$.	Found.
N	14.93	14.87

The picrate consists of light yellow needles melting with decomposition at 157°–158°. It is soluble in hot alcohol, hot water, or warm benzene, but insoluble in ether or ligroin, and only slightly soluble in cold water.

Synthesis of 1-Phenyl-2-methyl-3-furyl-5-pyrazolone.

Hydrochloride from Methylphenylhydrazine.—To 1.5 grams of furoylacetic ester was added 0.7 gram of methylphenylhydrazine obtained by decomposing the oxalate with potassium hydroxide, extracting with ether and evaporating the dried extract until all the ether had boiled off. After heating 20 minutes on the steam bath no apparent action took place, as the mixture retained its fluidity. On heating on an oil bath at 150° the mixture began to boil after a short time, and the heating was continued until ebullition ceased, when, on cooling, the oil became very viscous but would not solidify. It was then dissolved in chloroform, dried with calcium chloride and saturated with dry hydrochloric acid. On adding ether a precipitate of light brown crystals separated which crystallized from ethyl acetate and a little alcohol in transparent prisms melting with decomposition at 196°–197°. The substance is very soluble in alcohol, slightly soluble in chloroform and hot ethyl acetate and insoluble in ether. Water hydrolyzed it to an oil. With nitrous acid in slightly acid solutions it gives a green, crystalline, nitroso derivative, which changes in strongly acid solution to a red compound, but can be changed to the green again by diluting or making alkaline. From the crystalline form, melting point, solubility and reaction with nitrous acid, it is evident that the substance obtained by the action of symmetrical methylphenylhydrazine on furoylacetic ester is identical with the hydrochloride of 1-phenyl-2-methyl-3-furyl-5-pyrazolone described above.

1-Phenyl-2-methyl-3-furyl-4-nitroso-5-pyrazolone,



—To a solution of the hydrochloride of

1-phenyl-2-methyl-3-furyl-5-pyrazolone in dilute alcohol, hydrochloric acid and sodium nitrite were added; if an excess of hydrochloric acid was used a red compound separated, but if water was added to this or the amount of sodium nitrite was increased the precipitate became bright green and this green form was soon found to be the true nitroso derivative of the base, the red form being its hydrochloride. By crystallizing from dilute alcohol this substance was obtained pure. It was dried for analysis *in vacuo*.

0.1472 gram of the substance gave 20.42 cc. N at 22°.4 and 763 mm.

	Calculated for $C_{14}H_{11}O_3N_3$.	Found.
N	15.61	15.74

This nitroso compound crystallized from dilute alcohol in glistening green needles melting at 185° with decomposition. It is soluble in hot alcohol, hot benzene, or hot water, but insoluble in the cold solvents and only very slightly soluble in ether. Acids turn it red, the green color being restored by alkalies or even on diluting with water. On standing with alkalies it is decomposed as shown below.

Four grams of the nitroso derivative were heated on the steam bath with a strong solution of caustic potash until all the nitroso derivative had disappeared and drops of a brown oil collected on the bottom of the dish; the liquid and oil were then transferred to a flask and distilled with steam until no more oil came over. This distillate, which reduced Fehling's solution readily, was extracted with ether, the extract dried over potassium hydroxide and the ether evaporated, leaving a yellow oil. To some of this in alcohol solution a few drops of dilute sulphuric acid were added, when, on scratching the vessel, a white precipitate of very small crystals separated which were washed with alcohol and ether and dried. Under the microscope they appeared as very small rectangular plates melting at 180° with decomposition. On adding oxalic acid, the oil was converted into the oxalate of methylphenylhydrazine, a white precipitate of very small needles.

Some of the oil was heated with mercuric oxide, when, it turned brown and a peculiarly disagreeable smell,

the same as that of diazomethylphenyl prepared from methylphenylhydrazine in a similar manner, was given off. From these reactions it is evident that the oil obtained by the breaking down of the nitroso derivative of 1-phenyl-2-methyl-3-furyl-5-pyrazolone is symmetrical methylphenylhydrazine, and that the methyl group of this pyrazolone is in the position we assigned to it.

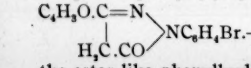
Hydrochloride, $C_{14}H_{11}O_3N_3HCl$.—Into a hot alcohol solution of the nitroso derivative described above, gaseous hydrochloric acid was passed until a precipitate began to form. The color of the solution changed from green to red and on cooling small red needles were deposited which were washed with ether and dried for analysis *in vacuo* over caustic potash.

0.2075 gram of the substance gave 0.0949 gram AgCl.

	Calculated for $C_{14}H_{12}O_3N_3Cl$.	Found.
Cl	11.62	11.31

The hydrochloride crystallizes in small bright red needles, but changes with extreme ease to the original green base. Even absolute alcohol effects the change unless a little hydrochloric acid is added to it. Once formed and kept perfectly dry, however, the hydrochloride is fairly stable. It decomposes at 189°.

1-p-Bromphenyl-3-furyl-5-pyrazolone,



NC_6H_4Br.—*p*-Bromphenylhydrazine reacts on the ester like phenylhydrazine. To 2 grams of the ester were added 2 grams of bromphenylhydrazine and the mixture heated on the oil bath to 120° for half an hour. The reaction product, a thick dark oil which on cooling solidified to a brown crystalline mass, was thoroughly washed with ether. This left a white powder which was crystallized from benzene-ligroin. It was dried for analysis *in vacuo*.

I. 0.1942 gram substance gave 0.1178 gram AgBr.

II. 0.1718 gram substance gave 14 cc. N at 21°.8 and 767 mm. pressure.

	Calculated for $C_{13}H_9O_2N_2Br$.	Found.
Br	26.23	25.81
N	9.18	9.33

This pyrazolone crystallizes in small white needles melting at 160°–161°. It is soluble in hot benzene or warm alcohol, but insoluble in ether, ligroin or water. Alkalies dissolve it readily and from their solutions it may be thrown down by acidifying; strong acids do not dissolve it. With nitrous acid it gives a red nitroso derivative and with ferric chloride a green precipitate.

1-p-Sulphonylphenyl-3-furyl-5-pyrazolone.—The free *p*-sulphonylphenylhydrazine does not react with the ester readily, but its sodium salt, on the contrary, behaves like all the other free hydrazines. Equal weights of the ester and sodium hydrazine-*p*-sulphonate prepared according to the method of Gallinek and von Richter[1] were heated on an oil bath to 170°, until the pasty mass at first formed was completely solidified. This product, the sodium salt of the pyrazolone, was washed with ether to remove any excess of ester, dissolved in water and acidified with dilute sulphuric acid, when a precipitate of brownish needles separated, which was filtered and crystallized from water after boiling with boneblack to remove the color.

I. 0.4005 gram of the substance, dried at 90° for 2 hours, lost 0.0210 gram when dried at 130°–140°.

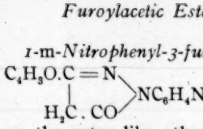
II. 0.2515 gram of the substance, dried *in vacuo*, gave 0.1795 gram $BaSO_4$.

	Calculated for $C_{13}H_{10}O_2N_2SO_3H.1H_2O$.	Found.
H_2O	5.56	5.24
S	9.87	9.80

This pyrazolone crystallizes from water in small square plates, which turn brown on standing. It is slightly soluble in hot alcohol and insoluble in ether, benzene, or chloroform. With nitrous acid it gives a red color, but does not give the "pyrazole blue" reaction. Alkalies dissolve it readily and from its alkaline solution it is reprecipitated by acids. It blackens but does not melt at 295°.

[1] Ber. d. chem. Ges., **18**, 3172.

1-m-*Nitrophenyl-3-furyl-5-pyrazolone*,



$C_4H_3O.C=N$, $H_2C.CO$, $NC_6H_4NO_2$. — *m*-Nitrophenylhydrazine reacted on the ester like other hydrazines. Two grams of the ester were heated in an oil bath with 1.6 grams of *m*-nitrophenylhydrazine. After heating one hour, the mixture had completely solidified to a brown mass which was washed with ether and crystallized from a benzene-ligroin mixture. It was dried *in vacuo* for analysis:

0.1701 gram of the substance gave 22.05 cc. N at 11°.4 and 766 mm.

	Calculated for $C_{13}H_9O_4N_3$.	Found.
N	15.49	15.55

This pyrazolone crystallizes in small, thick, yellowish brown prisms, which are the prevailing form if the solution is kept perfectly quiet; if the crystallizing solution is stirred foliated crystals are obtained. The melting point is 174°–175°. The substance is soluble in hot benzene or hot alcohol, but insoluble in the cold solvents or in ether, ligroin or water. Sodium hydroxide dissolves it on warming; hydrochloric acid does not dissolve it. With ferric chloride a greenish brown color is obtained and with nitrous acid a red solution.

1-Phenyl-5-furyl-3-pyrazolone, $C_4H_3OC—N—C_6H_5$, $HC.CO$, NH.—To 5 grams of the ester mixed with 4.2 grams of symmetrical acetphenylhydrazide were added 6 grams of phosphorus trichloride in small portions and the mixture was heated on a steam bath until the reaction was completed, which could be ascertained by the cessation of the evolution of hydrochloric acid. The reaction product, a thick purplish red syrup, was poured into strong ammonia when a dark oil separated out. The solution was extracted with ether and made barely acid when a precipitate of brown flakes was formed. This was filtered off and crystallized from 60 per cent. alcohol until it had a constant melting point. The yield was small,

amounting to only 0.5 gram of the pure product. The substance was dried *in vacuo*.

I. 0.2071 gram gave 0.5241 gram CO_2 and 0.0821 gram H_2O.

II. 0.2086 gram gave 22.51 cc. N at 23°.5 and 772 mm.

	Calculated for $C_{13}H_{10}O_2N_2$.	Found. I.	II.
C	69.03	69.01	...
H	4.42	4.40	...
N	12.39	....	12.31

This pyrazolone crystallizes in long, transparent prisms with square ends, which melt at 176°. It is slightly soluble in cold alcohol, readily in the warm solvent, fairly soluble in ether or in cold benzene, but insoluble in hot or cold water. Alkalies and concentrated acids dissolve it readily. With nitrous acid it gives a green nitroso derivative, but it does not give the "pyrazole blue" reaction.

The nitroso derivative was prepared by adding sodium nitrite to a hydrochloric acid solution of the pyrazolone. The color, which is at first orange, rapidly turns green and green flakes separate. The precipitate is fairly soluble in cold water and is turned red by acids.

SUMMARY.

The results of this research may be summarized as follows:

1. The properties and reactions of furoylacetic ester have been studied and show that this ester behaves like benzoyl- and acetacetic esters in most of its reactions. A new method for the synthesis of the ester has been tried and found to give better yields than the one previously used.

2. The action of hydroxylamine on the ester has been shown to take place in accordance with Abegg's theory and contrary to Hantzsch's views.

3. The 3- and 5-pyrazolone derivatives of furoylacetic ester have been studied and shown to give the usual reactions of the pyrazolones except as to the "pyrazole blue" reaction. A new homologue of antipyrine has been synthesized.

We are indebted to the Cyrus Warren Fund for some of the materials used in this research, for which we wish to express our gratitude.

Thanks are also due to Professor Charles Loring Jackson for his kindness in revising the manuscript.

ADDITIVE POWER OF 2-PENTENE.

By Roger F. Brunel and Eugene G. Probeck.

Facts have long been known which showed that a wide difference exists in the additive power toward acids of the hydrocarbons of the ethylene series. This subject was recently discussed from the standpoint of the theories of Michael.[1] It was shown that with a certain member of the series, isobutene, a maximum additive power is observed, and the occurrence of this maximum, as well as the differences in additive power of those members examined, was explained from a theoretical standpoint.

These differences in the additive power of the unsaturated C : C group must, obviously, be due to the number and position of the other atoms in the molecule. Comparison of a large number of compounds of the aliphatic series led Michael to the adoption of the following hypothesis[2] regarding the relation between the position of the atoms and their influence on each other: The atom under discussion, in the above case one of the unsaturated carbon atoms, is numbered one, and the others then numbered according to their degree of removal as the various chains of atoms are followed out. The mutual influence between atom number 1 and the various other atoms of the molecule will then decrease according to the following scale:

$$2\text{-}3\text{-}5\text{-}6\text{-}4\text{-}7\text{-}(9\text{-}10\text{-}11)\text{-}8.$$

It is to be emphasized that the influence of an atom in position 2 or 3 is much greater than that of a similar atom less

[1] Michael and Brunel: This Journal, **41**, 118 (1909).

[2] J. prakt. Chem., N. F., **60**, 335.

closely connected. It appears that the relative importance of the different positions is correctly represented by this scale, as it has been found to apply not only in the case of the alkenes, but in many other cases examined by Michael.[1] This is true, however, only as regards their position; the value of atoms in the various positions could be expressed quantitatively only roughly. It would plainly be of interest to determine their value exactly for some class of compounds, and with this object in view one of the authors has undertaken the examination of the additive power of some hydrocarbons not dealt with in the former article. The end can, of course, be reached only by the comparison of a considerable number of compounds. The hydrocarbon so far examined is 2-pentene, $H_3CCH:CHCH_2CH_3$, which is simply related to trimethylethylene and to 1-butene, with which it has been compared.

Since the addition of a compound consisting of two different atoms or groups to 2-pentene may give rise to two different compounds it is first necessary to determine which of these is chiefly formed. This question was investigated by Wagner and Saytzeff.[2] The hydrocarbon was treated with hydriodic acid, the product converted into alcohol, and this oxidized to the ketone, which was shown to consist, largely, at least, of methylpropyl ketone. From theoretical considerations we may conclude that this should be the chief product, while a small amount of the diethyl derivative probably formed would have escaped detection by their method. An examination of the formula will show what results should be expected.

Certain assumptions underlying the entire argument must first be recalled. The compound which is added to the hydrocarbon is in all cases an acid or water, which can be represented by HX, the halogen acids being a typical example. The relative attraction of the two carbon atoms for H and X will determine which of the two possible products will be formed, and any difference in the affinity of these two

[1] Ber. d. chem. Ges., **39**, 2138–2195, and in various other articles as well.
[2] Ann. Chem. (Liebig), **179**, 313 (1876).

carbon atoms must be the result of the influence of the atoms in the molecule. The hydrogen atoms are probably the chief factor, and in view of the strong affinity of hydrogen for negative radicals, Br, SO_4, OH, etc., we should expect that carbon atom to have the strongest attraction for the radical X which is most under the influence of the hydrogen atoms of the molecule; this carbon atom will have correspondingly less tendency to combine with another hydrogen atom. The question as to which of the two possible isomeric products will be formed is therefore to be settled by summing up the influences of the hydrogen atoms on the two unsaturated carbon atoms in the light of the above scale. This process consists merely of adding together the numbers of hydrogen atoms in the positions 2, 3, 4, etc., with respect to each of the carbon atoms.

The result of the application of this process to 2-pentene is as follows:

$$\text{I.}\quad \overset{4}{\underset{3}{H_3}}\overset{3}{\underset{2}{C}}—\overset{2}{\underset{3}{CH}}:\overset{1}{\underset{2}{CH}}—\overset{2}{\underset{3}{CH_2}}—\overset{3}{\underset{4}{CH_3}} \qquad \Delta^{\beta}—\overset{2}{C}—\overset{3}{\underset{5}{HH_4}}\overset{4}{H_2}\overset{5}{H_3}$$

$$\Delta^{\gamma}—\overset{2}{C}—\overset{3}{\underset{6}{HH_3}}\overset{4}{H_6}$$

The figure above or below each letter indicates the position and the one at the right the number of atoms in that position. Removing from each list the atoms common to both we obtain: $\Delta^{\beta}—\overset{3}{C}—\overset{5}{HH_3}$, $\Delta^{\gamma}—\overset{4}{C}—H_4$. It thus appears, after eliminating influences which are the same toward both unsaturated carbon atoms, that with respect to the γ-carbon atom there are four hydrogen atoms in position 4, while with respect to the β-carbon atom they are in positions 3 and 5. As a result the β-carbon atom will show a markedly greater affinity for the negative radical,[1] and correspondingly less for the hydrogen. The chief product will therefore be the compound $H_3CCH_2CH_2CHXCH_3$ (to the extent, perhaps, of 70–80 per cent.). We shall estimate the rate of addition on

[1] Whether the negative radical is drawn toward this point in the molecule because the force exerted by this carbon atom upon it is actually greater, or whether it is due to the force exerted by the hydrogen atoms themselves toward it, is probably open to question. The result here is the same from either point of view, and the above manner of expression appears to be best in accordance with the facts.

the basis of the formation of this only. Since a certain amount of the other product, $CH_3CH_2CHXCH_2CH_3$, is being formed simultaneously, the rate of addition will always be a little greater than it would be if all the hydrocarbon had to be disposed of through formation of the former product, and this must be kept in mind.

Assuming, then, that a 2-substituted normal pentane is to be the chief product, we may compare this hydrocarbon with 1-butene to see in which the addition should occur most readily, estimating first the force which will be exerted toward the negative group by that carbon atom with which it is to unite, then that toward the hydrogen. In the case of 1-butene the secondary derivative is practically the only product formed.[1]

II. $\overset{4}{\underset{5}{H_3C}}\!\!-\!\!\overset{3}{\underset{4}{CH_2}}\!\!-\!\!\overset{2}{\underset{3}{CH}}\!=\!\overset{3}{\underset{2}{CH_2}}$; III. $\overset{3}{\underset{4}{H_3C}}\!\!-\!\!\overset{2}{\underset{3}{CH}}\!=\!\overset{1}{\underset{2}{CH}}\!\!-\!\!\overset{2}{\underset{3}{CH_2}}\!\!-\!\!\overset{3}{\underset{4}{CH_3}}$.

By the addition process explained above we can compare the Δ^β-carbon of (II) with the Δ^β-carbon of (III) as follows:

II. $\Delta^\beta\!-\!C\!-\!\overset{2}{H}\,\overset{3}{H_4}\,\overset{4}{H_3}$ or II. $\Delta^\beta\!-\!C\!-\!\overset{4}{H}$;

III. $\Delta^\beta\!-\!C\!-\!\overset{2}{H}\,\overset{3}{H_4}\,\overset{4}{H_2}\,\overset{5}{H_3}$ III. $\Delta^\beta\!-\!C\!-\!\overset{5}{H_3}$.

Comparing the Δ^α-carbon of (II) with the Δ^γ-carbon of (III):

II. $\Delta^\alpha\!-\!C\!-\!\overset{2}{H_2}\,\overset{3}{H}\,\overset{4}{H_2}\,\overset{5}{H_3}$ or II. $\Delta^\alpha\!-\!C\!-\!\overset{2}{H}\,\overset{5}{H_3}$;

III. $\Delta^\gamma\!-\!C\!-\!\overset{2}{H}\,\overset{3}{H_3}\,\overset{4}{H_6}$ III. $\Delta^\gamma\!-\!C\!-\!\overset{3}{H_2}\,\overset{4}{H_4}$.

The first comparison indicates that the attraction for the negative group will be greater in the butene than in the pentene, due to the presence of three hydrogen atoms in the position 5 as against one in the position 4 in the butene. In considering the attraction for the hydrogen atom we must take into account the facts presented in the paper of Michael and Brunel[2] pertaining to the occurrence of a maximum in additive power with isobutene. The presence of hydrogen atoms in

[1] Lieben and Rossi: Ann. Chem. (Liebig), **158**, 166 (1871). A. and M. Saytzeff: J. prakt. Chem., N. F., **3**, 88.

[2] This Journal, **41**, 118 (1909).

the molecule increases the attraction of the unsaturated carbon atoms for the negative part of the addendum, but at the same time decreases it for the hydrogen. It is evident that the former factor is the controlling one in the lower members, where the additive power increases with the number of carbon and hydrogen atoms, but that as the size of the molecule increases the latter factor predominates. After passing beyond isobutene, although the affinity for negative atoms such as the halogens undoubtedly increases, as shown by the avidity with which halogen addition products are formed, the tendency to add halogen acids or sulphuric acid may be expected to decrease, as previously shown by our experiments. This does not mean that any amylene will react less readily than any butene. Isobutene reacts the most readily of the alkenes, but if trimethylethylene is compared with pseudobutene the greater reactivity is shown by the former, in which the conditions are especially favorable to addition; and the expected decrease would then appear in the next step to the hexene series. We may say, however, that beyond the butene series any alkene is likely to form addition products with acids less readily than a member of the next lower series unless, through its structure, it offers conditions *much more* favorable for the addition than does the other.

In 2-pentene the attraction for the negative group is considerably greater than in 1-butene, as shown above. The attraction for hydrogen is also, as shown, somewhat less, although the difference here appears to be smaller than the former one, so that, from this consideration alone, we should look for greater additive power in the pentene, although the difference should not be great. If, however, we bear in mind the fact that with the transition from the C_4 to the C_5 series the relative importance of the latter factor, the reduction in the affinity for hydrogen, increases, it will appear quite possible that the amylene should show the weaker additive power, as has been found to be the case, the ratio butene : amylene being about 7 : 5.

The comparison of 2-pentene with trimethylethylene is also

of interest. In the formulas the predominant course of the addition is indicated by the letters in parentheses.

IV. V. $H_3C.\overset{(X)}{C}H : \overset{(H)}{C}H.CH_2.CH_3$.

An examination of these formulas will show that the carbon atoms which combine with hydrogen are subject to the same influence in the two cases, the numbers of hydrogen atoms in the various positions being identical. All of the difference in additive power must then lie in the degree of attraction for the negative radical. This difference is caused chiefly by a change in the position of one methyl group. In (IV) it is in position 2,3 with respect to the carbon atom which unites with the negative group, while in (V) it is in position 4,5. The only other difference is the removal of a hydrogen atom from position 4 in (IV) to position 2 in (V). These two factors are in opposition to each other, but the first is the greater, and the results of this comparison should give us, for this particular case at least, an estimate of the relative values or influences of hydrogen atoms in the positions 3 and 5. The difference appears to be considerable, as the velocity with which trimethylethylene dissolves in dilute sulphuric acid is over one hundred times as great as for 2-pentene.

It is obvious that this method of comparing the hydrocarbons is open to the objection that in the heterogeneous system with which we are dealing differences in the merely physical solubility of the hydrocarbons in the aqueous acids used would exert great influence on the results. It does not appear that these differences should be very great, and, even if they were the chief factor, these great differences in solubility with such small changes in structure would be of little less interest than differences in reactivity toward the acids used. One of the authors intends to examine, in the near future, the solubility in water of some of the hydrocarbons used.

EXPERIMENTAL PART.

Diethylcarbinol was prepared according to the Grignard method. One hundred and nine grams ethyl bromide were

added to 24 grams magnesium in anhydrous ether. The ethyl bromide was added as fast as possible, the flask, after the reaction had begun, being placed in a mixture of ice and salt and shaken continuously. A few minutes' heating nearly completed the solution of the magnesium. Thirty-eight grams ethyl formate were then added, and the whole was allowed to stand an hour, then boiled thirty minutes and worked up in the usual manner. The product was dried with potassium carbonate and fractionated with a short column of beads. Seventeen grams were obtained distilling at 112°–113°, and 11.5 grams at 113°–113°.5, these together making a yield of 63 per cent.[1]

Diethylcarbinyl iodide was prepared by passing hydriodic acid gas into the carbinol at 0°. When the saturated solution was allowed to come to room temperature two layers were formed, the upper of which was washed with carbonate, dried, and fractionated. Nineteen and eight-tenths grams were obtained boiling at 142°–144° and 40.3 grams at 144°–146°.

2-Pentene was prepared by the method of Wagner and Saytzeff[2] by treating the iodide with alcoholic potash and distilling off the low-boiling product. From 60 grams of iodide 17.5 grams of hydrocarbon were obtained. After two fractionations with beads 13.2 grams were obtained boiling at 37°–39°.

1-Butene was prepared by the method described by Butlerow[3] for isobutene, the yield, as already noted, being poor.

Comparison of 2-Pentene and 1-Butene.—1-Butene, boiling at —5°, was condensed and sealed in a tube with 1 cc. of dilute sulphuric acid, the amount being determined by weighing before and after its introduction, and an equal amount of the amylene was then sealed in a similar tube. In the table below, in the last column, are given the times that would have been required for solution of the butene if equimolecular amounts of the two had been taken.

[1] More recently yields of 75-80 per cent. have been obtained. An excess of 5–10 per cent. of ethyl bromide is usually added to complete the solution of the magnesium as quickly as possible.

[2] Ann. Chem. (Liebig), **175**, 373 (1875).

[3] Z. Chem., **13**, 238 and 544 (1870). Ber. d. chem. Ges., **3**, 622 (1871).

Pts. acid to 1 pt. water.	Wt. of hydrocarbon. Gram.	Time of solution of 2-Pentene. Minutes.	Time of solution of 1-Butene. Minutes.	Time for 1-butene with equimol. amount. Minutes.
3.0	0.0319	135	121	97
3.5	0.0342	130	118	94

The additive powers of 2-pentene and 1-butene are therefore nearly in the ratio of 5:7.

Comparison of 2-Pentene and Trimethylethylene.—Small sealed tubes were prepared, each containing 0.040 gram of hydrocarbon and a large excess of dilute sulphuric acid. These were placed on the shaking machine and the time required for complete solution of the hydrocarbon noted. The results are given in the following table:

Mols. of H_2SO_4 to one of hydrocarbon.	Parts of acid to one part of water.	Time of solution	
		Amylene.	Trimethylethylene.
15	1.5	Not dissolved after 23 hours	10 mins.
15	2.0	7 hrs. 54 min.	At once
15	3.0	2 hrs. 17 min.	At once
15	3.5	2 hrs. 8 min.	At once

[Contributions from the Chemical Laboratory of Harvard College.]

A METHOD FOR PURIFYING AND DRYING ORGANIC LIQUIDS BY WIPING.

By C. Loring Jackson and A. H. Fiske.

In the course of a research on curcumine, carried on by Dr. Latham Clarke and one of us, it became necessary to determine the nature of 2 or 3 drops of an organic oil, which was obtained mixed with hydriodic acid. As there was too little to dry and distil in the ordinary way, and, owing to its volatility, we were afraid to dry it in a desiccator, we were obliged to find some other method for bringing it into a state fit for analysis, and hit upon the plan of drying it by wiping with strips of moist filter paper, after the hydriodic acid had been removed by washing. This method seemed to work so well that we decided to test it by further experiments, and now describe it for the benefit of others who, like us, have not found

in the literature any way of dealing with a case like this. We selected as the substance for our experiments commercial chloroform, which gave the following results on analysis:

I. 0.2041 gram substance gave 0.7263 gram AgCl.
II. 0.1783 gram substance gave 0.6335 gram AgCl.

	Calculated for $CHCl_3$.	Found. I.	II.
Cl	89.13	87.98	87.86

It therefore contained a slight amount of impurity, probably water or alcohol.

In our first experiment, 0.2256 gram of this chloroform was washed with 0.1284 gram of water, which was shaken with it. Part of the water was then removed with a small pipette, and the rest with strips of filter paper about 5 mm. wide and creased lengthwise, so as to make them stiffer and easier to handle; these were moistened with water sufficiently to make them repel the chloroform, but were kept still dry enough to take up more water. The inside of the tube, both above and below the liquid, was wiped with these strips of paper until it seemed perfectly dry, and the chloroform was then analyzed (I) without any other drying. The chloroform lost during this treatment 0.0748 gram, or about 33 per cent. A second specimen (II) weighing 0.3023 gram, treated in the same way, lost 0.0854 gram, or about 28 per cent.

I. 0.1508 gram substance gave 0.5423 gram AgCl.
II. 0.2169 gram substance gave 0.7781 gram AgCl.

	Calculated for $CHCl_3$.	Found. I.	II.
Cl	89.13	88.92	88.69

These results show that the chloroform was dried sufficiently for all practical purposes by wiping it with slightly moist filter paper; and this conclusion is supported by the following analyses of volatile liquids obtained in the course of researches made in this laboratory, all of which were wiped in the manner described above.

0.2102 gram of methyl iodide obtained from curcumine gave 0.3454 gram AgI.

	Calculated for CH_3I.	Found.
I	89.43	88.84

I. 0.2943 gram of bromoform obtained in one of our researches gave 0.6560 gram AgBr.

II. 0.2391 gram gave 0.5339 gram AgBr.

	Calculated for $CHBr_3$.	Found. I.	Found. II.
Br	94.86	94.88	94.99

The following experiments were tried to see whether a substance dissolved in the chloroform could be removed to advantage by this method of wiping.

A. With 0.5193 gram of chloroform was mixed about 0.001 gram of iodine. After the iodine had completely dissolved, slips of filter paper moistened with a solution of 2 grams of potassic iodide in 10 cc. of water were immersed in the liquid until it had become colorless. It was necessary to use 8 pieces of paper to remove the last trace of the color. A drop of water was then added and shaken with the chloroform, which was afterward wiped dry with strips of slightly moist filter paper. The loss in all these processes was 0.3410 gram, or about 66 per cent.

B. With 0.5316 gram of chloroform was mixed about 0.001 gram of iodine as before, and the mixture shaken with successive drops of the iodide of potassium solution until the color was discharged, the solution being removed with a very small pipette. Nine treatments with the potassic iodide solution were necessary before the color disappeared. The loss of chloroform was 0.2801 gram, or about 53 per cent. The colorless liquid was wiped dry.

A. 0.1783 gram gave 0.6397 gram AgCl.

B. 0.2515 gram gave 0.9108 gram AgCl.

	Calculated for $CHCl_3$.	Found. *A.*	Found. *B.*
Cl	89.13	88.72	89.52

These analyses show that the wiping had removed all the dissolved iodine, whereas the washing was less efficient, a small amount of iodine or potassic iodide having been left in the

chloroform. The wiping was also more conveniently applied, and did its work completely in 8 applications, while the washing required 9 for only partial purification; on the other hand, the loss of chloroform was 60.9 milligrams greater with the wiping than with the washing.

It is obvious that a liquid cannot be dried completely by wiping it with slightly moist filter paper, but the experiments described show that the amount of water left in the substance is less than 0.5 per cent., and therefore usually not enough to interfere with the identification of the substance by analysis.

We feel justified in recommending this process for the purification and drying of the substance for analysis in the not uncommon cases where in an investigation it is necessary to determine the composition of a liquid obtained in too small quantity to be treated with a drying agent, followed by distillation, and too volatile to be dried to advantage *in vacuo*. One great point in its favor it that it takes only a few minutes instead of the hours needed for the older methods of drying; and in the case for which it was invented this rapidity of action was a great advantage, as the substance was decomposed by exposure to the air for 3 hours, so that here drying by wiping was not only more convenient, but also much safer, than the usual methods.

CAMBRIDGE, MASS.,
June 18, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXIV.—ALKYLATION OF AROMATIC AMINO ACIDS: NITRAMINO AND IODAMINO ACIDS.

[FOURTH PAPER.]

BY HENRY L. WHEELER AND CARL O. JOHNS.

We have now examined the behavior of 4-nitro-2-aminobenzoic acid (I), 4-amino-2-nitrobenzoic acid (II), 4-iod-2-aminobenzoic acid (IV), and 4,5-diiod-2-aminobenzoic acid (VI) when warmed with potassium hydroxide and an excess of alkyl iodide in alcoholic solution.

The silver salt of 4-nitro-2-aminobenzoic acid was found by Wheeler and Barnes[1] to give the *N*-alkyl compounds

$$C_2H_5NHC_6H_3(NO_2)COOH,$$

and, in smaller amount,

$$C_2H_5NHC_6H_3(NO_2)COOC_2H_5.$$

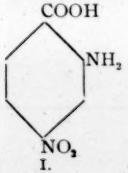
We find, with potassium hydroxide and ethyl iodide, that this acid gives a mixture of 40 per cent. of the primary amino ester,

$$H_2NC_6H_3(NO_2)COOC_2H_5,$$

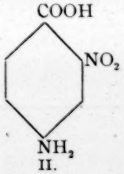
about 40 per cent. of the N-alkyl acid,

$$C_2H_5NHC_6H_3(NO_2)COOH,$$

and 20 per cent. of unaltered acid. In other words, there appears to be about an equal tendency for the potassium salt of this acid to give *N*- and *O*-ethyl derivatives.



I.



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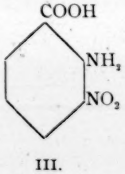


III.

When 2-nitro-4-aminobenzoic acid (II) was treated in the same manner we obtained only the primary *O*-ester,

$$H_2NC_6H_3(NO_2)COOC_2H_5,$$

(43.4 per cent.) and the unaltered acid (48.3 per cent.). These results are precisely opposite to what would be expected from the theory of stereochemical interference, since 2-nitro-4-aminobenzoic acid should give a *N*-derivative more readily than 4-nitro-2-aminobenzoic acid, the latter acid having the carboxyl adjacent to the $-NH_2$ group.

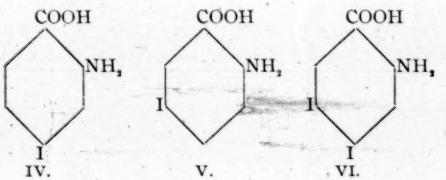
It appears that substituted *o*-aminobenzoic acids give *N*-derivatives more readily than the isomeric *p*-aminobenzoic acids; however, in this series the potassium salt of 3-nitro-2-aminobenzoic acid (III) gives an *O*-ester.[2]

The influence of position and negative character of substit-

[1] This Journal, **20**, 217 (1898).

[2] Zacharias: J. prakt. Chem., **43**, 437 (1891).

uents, in the absence of stereochemical interference, can now be compared in the following series: 4-Iod-*o*-aminobenzoic acid (IV), 5-iod-*o*-aminobenzoic acid (V), and 4,5-diiod-*o*-aminobenzoic acid (VI).



IV. V. VI.

Both 4-iod-*o*-aminobenzoic acid and 5-iod-*o*-aminobenzoic acid[1] gave 71–76 per cent. of *N*-alkyl acids and no *O*-esters were observed, while 4,5-diiod-*o*-aminobenzoic acid alkylated with difficulty and gave an *O*-ester (28 per cent.) along with unaltered acid.

Since 4,5-diiod-*o*-aminobenzoic acid gives an *O*-ester it is not necessarily due to stereochemical interference that 3,5-diiod-*p*-aminobenzoic acid[2] and especially 3,5-diiod-*o*-aminobenzoic acid[3] give esters and not *N*-derivatives by the above treatment.

These results show conclusively that the tendency of amino acids to react in an abnormal manner and give esters is not dependent on stereochemical interference.

EXPERIMENTAL PART.

2-Amino-4-nitrobenzoic Acid.—This acid was first prepared by Wheeler and Barnes.[4] We have improved the yield by the use of magnesium sulphate and by proceeding as follows: Thirty-five grams of 4-nitro-*o*-acettoluide were suspended in a liter of hot water and 90 grams of crystallized magnesium sulphate were added. Steam was passed into this mixture, in a large bottle, and 90 grams of potassium permanganate in 2 liters of hot water were added in portions from time to

[1] Wheeler and Johns: THIS JOURNAL, **42**, 403 (1910).
[2] Wheeler and Liddle: *Ibid.*, **42**, 455 (1909).
[3] Wheeler and Johns: *Loc. cit.*
[4] THIS JOURNAL, **20**, 219 (1898).

time. The oxidation was complete in less than three hours. The manganese dioxide was then filtered off, well washed with hot water, and the total filtrates were evaporated to about 500 cc. The solution was made distinctly alkaline with ammonia and filtered. On acidifying with hydrochloric acid, a bulky precipitate of the acetamino acid separated. This was filtered off and dissolved in 200 cc. of alcohol containing 15 cc. of concentrated sulphuric acid. When this solution was digested on the steam bath the free acid separated as a bright, orange, crystalline precipitate. The yield, on diluting the solution with water, was 88 per cent. of the calculated. The acid melted at 264°, as previously described.

Ethyl 2-amino-4-nitrobenzoate was prepared by Wheeler and Barnes, but the melting point of the substance was not given.

We have prepared the ester by boiling the acid in alcoholic solution containing a little sulphuric acid. After evaporating most of the alcohol the residue was treated with dilute ammonia and crystallized from alcohol. It formed orange-colored prisms with rectangular ends and it melted to an oil at 100°. It was very soluble in ether and hot alcohol.

	Calculated for $C_9H_{10}O_4N_2$.	Found.
N	13.33	13.27

Action of Ethyl Iodide upon Potassium 2-Amino-4-nitrobenzoate.—Five grams of the acid were dissolved in 75 cc. of alcohol containing 1.6 grams of potassium hydroxide (one molecule). To this 6 grams of ethyl iodide were added. The mixture was heated for 2 hours under a return condenser, whereupon the solution became acid to litmus. It was evaporated to dryness and the residue was treated with dilute ammonia. This left 2.3 grams of insoluble substance which, when crystallized from alcohol, resembled the oxygen ester above in every respect and when mixed with it the mixture melted sharply at 100°. The yield of ester was 40 per cent. of the calculated.

When the ammonia solution, obtained above, was acidified with hydrochloric acid it gave a precipitate which weighed 4.3 grams. This was a mixture of unaltered acid and the

N-ethyl acid. The unaltered acid was isolated by crystallizing from alcohol. It was identified by its melting point and the following analysis:

	Calculated for $C_7H_6O_4N_2$.	Found.
N	15.38	15.16

The alcoholic mother liquors from which the unaltered acid had been isolated were concentrated and by fractional crystallization from alcohol the *N*-ethyl acid was isolated in the form of golden yellow plates. This substance was identical with the acid described by Wheeler and Barnes and when esterified it gave the ethyl ester melting at about 80°. It was impossible to get the exact yield of the *N*-ethyl acid, but it was estimated to be about 40 per cent. of the calculated.

	Calculated for $C_9H_{10}O_4N_2$.	Found.
N	13.33	13.56

Attempts were made to introduce iodine into 4-nitranthranilic acid in the same manner as proved successful in the case of anthranilic acid, but it was found that after digesting the aqueous solution of the potassium salt with iodine on the steam bath the acid was recovered unaltered. An attempt to iodate the acid by means of iodine monochloride also failed.

2-Iod-4-nitrobenzoic Acid.—Eight grams of 2-amino-4-nitrobenzoic acid were dissolved in 100 cc. of 40 per cent. sulphuric acid and 4 grams of sodium nitrite were added to the cold solution. After a few minutes the mixture was poured on crushed ice, giving a clear solution. Ten grams of potassium iodide were added and the mixture was heated on the steam bath, the excess of iodine being removed by means of sodium bisulphite. The yield was 99 per cent. of the calculated.

The iodnitro acid was very soluble in ether, benzene, alcohol, chloroform or acetone and difficultly soluble in ligroin or carbon tetrachloride. It dissolved sparingly in hot water and separated on cooling partly as an oil that soon solidified and partly as long slender prisms which melted at 143°. Its solution in ammonia was precipitated by hydrochloric acid:

	Calculated for $C_7H_4O_4NI$.	Found.
N	4.77	4.66

2-Iod-4-aminobenzoic Acid.—Two grams of 2-iod-4-nitrobenzoic acid were dissolved in 25 cc. of concentrated ammonia. This solution was mixed with one containing 12.2 grams of ferrous sulphate in 50 cc. of water. There was a slight evolution of heat and reduction took place rapidly. The mixture was heated on the steam bath and filtered after 5 minutes. The filtrate was evaporated to dryness and the residue extracted with alcohol. On evaporating the alcohol and treating with a little water, 73 per cent. of the calculated amount of the amino acid was obtained.

This iodamino acid was easily soluble in ether or alcohol and difficultly soluble in benzene, but dissolved slightly in hot water. It dissolved in dilute alkali and was precipitated by hydrochloric acid. When crystallized from dilute alcohol it formed colorless needles that effervesced at 180°:

	Calculated for $C_7H_6O_2NI$.	Found.
N	5.32	5.22

When an attempt was made to iodate this acid by treating the material in glacial actic acid with iodine monochloride, a dark solution resulted and when diluted with water and made alkaline with ammonia a black, sticky tar was obtained. This did not dissolve in alkali.

When the acid (2 grams) was treated with 4 molecular proportions of potassium hydroxide and 5 of ethyl iodide in alcoholic solution for 4 hours, an unpromising black tar was again obtained. This was not soluble in ammonia.

2-Nitro-4-acetaminobenzoic Acid.—This acid has recently been prepared by Bogert and Kropff[1] by nitrating *p*-toluidine, acetylating and oxidizing with potassium permanganate.

We started with 2,4-dinitrotoluene, partially reduced this with ammonium sulphide, acetylated and oxidized with potassium permanganate. The latter operation was carried out as described above in the case of the preparation of 2-amino-

[1] J. Am. Chem. Soc., **31**, 847 (1909).

4-nitrobenzoic acid. We can add to Bogert and Kropff's description that the best yield (74.2 per cent. of the calculated) of this acid was obtained when slightly less than three parts of potassium permanganate were used to one part of *o*-nitro-*p*-acettoluide.

The acid was soluble in alcohol and difficultly soluble in ether and boiling benzene. It was sparingly soluble in hot water, from which it crystallized in rectangular prisms. It melted to a brown oil at 217° with slight effervescence (Bogert and Kropff give 219°, corr.).

	Calculated for $C_9H_8O_5N_2$.	Found.
N	12.50	12.33

2-Nitro-4-aminobenzoic Acid.—Attempts to hydrolyze off the acetyl group from the above by means of either concentrated or dilute hydrochloric acid resulted in the formation of considerable quantities of *m*-nitraniline, along with more or less of the acid.

Bogert and Kropff used dilute sulphuric acid to remove the acetyl group or, better, a 10 per cent. solution of potassium hydroxide.

The hydrolysis was readily accomplished by means of normal potassium hydroxide. Ten grams of the acetyl acid were heated, with 200 cc. normal potassium hydroxide solution for one hour on the steam bath. The solution was cooled and then carefully precipitated with hydrochloric acid. The yield was 87 per cent. of the calculated.

The acid was easily soluble in alcohol and difficultly soluble in ether or benzene. It was moderately soluble in hot and but slightly soluble in cold water. It crystallized from dilute alcohol in bronze-colored leaflets composed of small crystals that decomposed with charring and effervescence at 232°.

A patent (D. R. P. No. 204,884) for the preparation of this acid has recently been taken out by the firm of Meister Lucius and Brüning, their method being the partial reduction of 2,4-dinitrobenzoic acid. The melting point 234°–235° is given, while Bogert and Kropff give 239°.5 (corr.).

	Calculated for $C_7H_6O_4N_2$.	Found.
N	15.38	15.25

Action of Ethyl Iodide upon Potassium 2-Nitro-4-aminobenzoate.

Ethyl 2-Nitro-4-aminobenzoate.—Twelve grams of *o*-nitro-*p*-aminobenzoic acid were dissolved in 200 cc. of alcohol containing 5 grams of potassium hydroxide, and 25 grams of ethyl iodide were added. The mixture was heated on the steam bath under a return condenser. The sodium salt separated and slowly dissolved again. The heating was continued for 5 hours, and after evaporating to dryness the residue was treated with water to remove potassium salts. This filtrate gave 3.3 grams of unaltered acid when acidified with hydrochloric acid. The portion not soluble in water was treated with dilute ammonia and 2.5 grams of unaltered acid were obtained on acidifying. The portion insoluble in ammonia weighed 6.0 grams, or 43 per cent. of the calculated. This was the ethyl ester. When crystallized from dilute alcohol it formed stout, elongated prisms, which melted at 130°. It was easily soluble in cold alcohol, ether and benzene, but almost insoluble in hot water.

	Calculated for $C_9H_{10}O_4N_2$.	Found.
N	13.33	13.46

The above ester was also formed by heating 10 grams of *o*-nitro-*p*-aminobenzoic acid in 120 cc. of absolute alcohol containing 2 cc. of sulphuric acid for 10 hours on the steam bath. Only 3.5 grams of ester were formed, which is 30.4 per cent. of the calculated yield. One and five-tenths grams of *m*-nitraniline were formed and 4 grams of unaltered acid were recovered.

2-Nitro-4-iodbenzoic Acid.—Ten grams of *o*-nitro-*p*-aminobenzoic acid were dissolved in 30 cc. of concentrated sulphuric acid. This was best accomplished by grinding the mixture in a mortar. Four and two-tenths grams of sodium nitrite were added and the mixture was poured on crushed ice, whereupon the whole dissolved to a clear yellow solution, which was added to an aqueous solution of 25 grams of potas-

sium iodide. A bulky, spongy, black mass was formed which soon hardened to a red powder. The mixture was warmed and the free iodine was removed with sodium bisulphite. The yield of crude material was 13 grams, or 81 per cent. of the calculated.

When crystallized from dilute alcohol the acid gave beautiful, diamond-shaped prisms, which melted to a clear oil at 192°. It was easily soluble in ether and alcohol, moderately soluble in boiling benzene, and almost insoluble in hot water.

	Calculated for $C_7H_4O_4NI$.	Found.
I	43.34	42.87
N	4.77	4.70

2-Amino-4-iodbenzoic Acid.—Eight grams of *o*-nitro-*p*-iodbenzoic acid were dissolved in 100 cc. of concentrated ammonia and 50 grams of ferrous sulphate dissolved in 200 cc. of water were added to this solution. After remaining for one hour the mixture was heated for 15 minutes on the steam bath and then filtered. The ferric hydroxide was washed with water and on evaporating the filtrates and precipitating with hydrochloric acid the yield of iodamino acid obtained was 89 per cent. of the calculated. The acid was easily soluble in cold alcohol or ether, difficultly soluble in benzene, and almost insoluble in water. When crystallized from dilute alcohol it formed colorless, flat prisms, pointed at both ends. It decomposed with charring at 208°.

	Calculated for $C_7H_6O_2NI$.	Found.
I	48.29	48.15

Action of Ethyl Iodide upon Potassium 2-Amino-4-iodbenzoate.

2-Ethylamino-4-iodbenzoic Acid.—Four grams of the above acid were dissolved in 40 cc. of 93 per cent. alcohol containing 0.9 gram of potassium hydroxide. Ten grams of ethyl iodide were added and the solution was heated on the steam bath for 1 hour and then evaporated to dryness. The solid residue was not soluble in water. It dissolved in dilute ammonia and when acidified with hydrochloric acid the precipitate obtained weighed 3.2 grams, or 72 per cent. of that calculated

for a *N*-ethylamino acid. It was easily soluble in ether or benzene, almost insoluble in hot water, and easily soluble in hot alcohol. It crystallized from alcohol in clusters of plates, which melted with effervescence at 188°.

	Calculated for $C_9H_{10}O_2NI$.	Found.
I	43.65	43.03

Action of Methyl Iodide upon Potassium 2-Amino-4-iodbenzoate.

2-Methylamino-4-iodbenzoic Acid.—Four grams of 2-amino-4-iodbenzoic acid were dissolved in 50 cc. of alcohol containing 0.9 gram of potassium hydroxide. Seven grams of methyl iodide were added and the mixture was heated for 1 hour under a return condenser, after which it was evaporated to dryness. The potassium iodide was dissolved out with water and the solution thus obtained gave no precipitate when acidified. There was therefore no potassium salt of the acid unacted upon. The portion insoluble in water dissolved readily in dilute ammonia and when precipitated with hydrochloric acid weighed 3.2 grams, or 76 per cent. of the calculated. The acid was easily soluble in ether or benzene and almost insoluble in boiling water. It was purified by dissolving in ether and filtering off a trace of black substance. The ether solution was evaporated to dryness and the residue was crystallized from alcohol. It then formed a bulky mass of needles that melted to an oil at 197°.

	Calculated for $C_8H_8O_2NI$.	Found.
I	45.84	45.83

2-Amino-4,5-diiodbenzoic Acid.—Five grams of 2-amino-4-iodbenzoic acid were dissolved in 75 cc. of water containing 1.5 grams of potassium hydroxide and 5 grams of powdered iodine were added. The mixture was shaken until practically all of the iodine had dissolved and a gray precipitate appeared. The excess of iodine was removed with sodium bisulphite and the precipitate filtered off. It weighed 6 grams, or 81 per cent. of the calculated.

This acid was readily soluble in ether or alcohol, moderately soluble in boiling benzene, and almost insoluble in hot water.

After treatment with ether a small amount of black substance could be removed by filtering. The solution was then evaporated to dryness and the residue was dissolved in 14 per cent. ammonia by warming. On cooling, the ammonium salt separated in clusters of colorless, pointed prisms. When the salt was dissolved in very dilute ammonia and the solution was acidified with hydrochloric acid, a white crystalline precipitate was obtained. This did not have a definite melting point but began to give off iodine above 200°, turning black and effervescing slightly at 210°–220°.

	Calculated for $C_7H_5O_2NI_2$.	Found.
I	65.23	65.03

3,4-Diiodbenzoic Acid.—Two grams of the above amino acid were dissolved in 50 cc. of alcohol containing 2 cc. of sulphuric acid. Two grams of sodium nitrite were added and the mixture was heated for a half hour on the steam bath. The resulting solution, on pouring into water, gave a bulky precipitate. This melted at about 255°, when crystallized from alcohol, and when mixed with a sample of 3,4-diiodbenzoic acid prepared by Wheeler and Liddle[1] the melting point was not altered.

2,4,5-Triiodbenzoic Acid.—Two grams of 2-amino-4,5-diiodbenzoic acid were dissolved in 20 cc. of concentrated sulphuric acid, the solution was cooled and 1.0 gram of sodium nitrite was added. This mixture was poured on cracked ice which had been moistened with concentrated hydrochloric acid. After the lapse of an hour the undissolved portion was filtered off and an aqueous solution of 5 grams of potassium iodide was added to the filtrate. A violent reaction ensued. After heating for a short time on the steam bath the excess of iodine was removed with sodium bisulphite and the triiod acid then appeared as a brick-red deposit. The pure acid was almost insoluble in hot water or benzene, moderately soluble in ether or hot alcohol. From the latter solvent it crystallized in small, colorless needles, which melted to an oil at 248°. The yield was 72 per cent. of the calculated.

[1] This Journal, **42**, 457 (1909).

	Calculated for $C_7H_5O_2I_3$.	Found.
I	76.20	75.90

Action of Ethyl Iodide upon Potassium 2-Amino-4,5-diiodbenzoate.

Ethyl 2-Amino-4,5-diiodbenzoate.—Two grams of 2-amino-4,5-diiodbenzoic acid were dissolved in 40 cc. of absolute alcohol containing 0.3 gram of potassium hydroxide. Two grams of ethyl iodide were added and the mixture was heated for one hour on a steam bath, at the end of which time it was acid to litmus. On evaporating to dryness and treating the residue with dilute ammonia 0.6 gram, or 28 per cent., of the calculated amount of ester remained undissolved. This was almost insoluble in hot water, but dissolved readily in ether or benzene, and was easily soluble in hot alcohol, from which it crystallized in slender prisms which melted to an oil at 137°. When warmed with dilute alkali it gave 2-amino-4,5-diiodbenzoic acid.

	Calculated for $C_9H_9O_2NI_2$.	Found.
I	60.91	60.15

Several attempts were made to get a better yield of ester by using 2 or 3 molecular proportions of potassium hydroxide and an excess of ethyl iodide, but the results were poorer than when the above proportions were used. The portion that did not esterify was identified as the unaltered acid and was used again to obtain more of the ester.

2-Amino-4,5-diiodbenzoic acid did not esterify to any marked extent with alcohol and sulphuric acid after heating for 5 hours. A small quantity of ester was obtained by dissolving 0.5 gram of the acid in alcohol and passing a stream of hydrogen chloride through the hot solution for an hour. It was identical with the product obtained by alkylating the potassium salt with ethyl iodide.

NEW HAVEN, CONN.,
July, 1910.

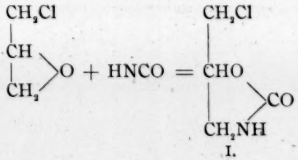
[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXV.—STUDIES IN THE OXAZOLE SERIES: THE ADDITION OF CYANIC ACID TO EPICHLORHYDRIN.

[SECOND PAPER.]

By Treat B. Johnson and Herbert H. Guest.

In 1878, A. L. Thomsen[1] investigated the behavior of silver and potassium cyanates towards epichlorhydrin. He observed that the silver salt had no action on this chloride, but that potassium cyanate reacted smoothly in aqueous solution, giving a crystalline substance, $C_4H_6O_2NCl$. He showed that this reacted with acetic anhydride, giving a monacetyl derivative, and also states that it underwent decomposition when warmed with a dilute solution of potassium hydroxide, giving potassium chloride, potassium carbonate and ammonia. When heated with concentrated hydrochloric acid at 150° carbon dioxide and ammonium chloride were formed and also, to quote from the original, "eine wenig einladende Substanz welche nicht in einem für die Analyse geeigneten Zustande erhalten werden konnte." Thomsen explained the formation of this compound by assuming a simple addition of cyanic acid to epichlorhydrin, and assigned to it, without further proof, the structure of a *ketotetrahydrooxazole* (I). The object of the work described in this paper was to



I.

synthesize Thomsen's compound by a new method and therefore determine the manner of addition of cyanic acid to epichlorhydrin.

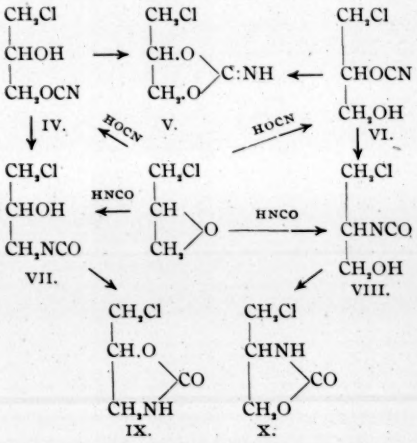
If we assume that cyanic acid can exist in two tautomeric forms, (II) and (III), and that it behaves in a dilute, aqueous

[1] Ber. d. chem. Ges., **11**, 2136.

HNCO
II.

HOCN
III.

solution as an electrolyte like hydrochloric acid, several unstable, intermediate products might be formed by its action on epichlorhydrin, according as it undergoes dissociation into H and NCO or H and OCN ions. It could add, theoretically, to this oxide in four ways, giving the unstable, acyclic cyanic and isocyanic esters (IV), (VI), (VII) and (VIII), which

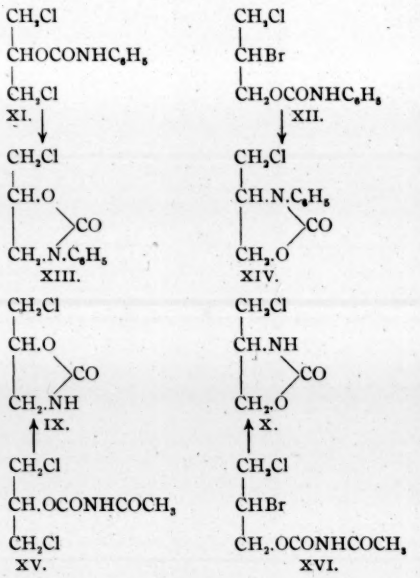


would then undergo rearrangements into the two isomeric ketotetrahydrooxazoles (IX) and (X). The cyanic esters (IV) and (VI), instead of rearranging to the isocyanates (VII) and (VIII), respectively, might also undergo metameric changes, giving the same imidocarbonate (V). Therefore three isomeric, cyclic compounds might theoretically be formed by the action of cyanic acid on epichlorhydrin, *viz.*, β-chlormethyl-μ-ketotetrahydrooxazole (IX),[1] α-chlormethyl-

[1] The writer desires to correct here a typographical error in the first paper of this series (THIS JOURNAL, **44**, 352). The ketotetrahydrooxazoles should be designated as μ-keto instead of ω-keto derivatives.

μ-ketotetrahydrooxazole (X), and α-chlorpropyleneglyceryl imidocarbonate (V).

In a previous paper from this laboratory Johnson and Langley[1] have described the phenylurethanes of all the haloid esters of glycerol containing chlorine and bromine. They observed that these compounds are especially characterized by their behavior in the presence of alkali, and undergo transformations into ketotetrahydrooxazoles with loss of a halogen acid. For example: β,β'-dichlorisopropyl phenylcarbamate (XI) and β-brom-γ-chlorpropyl phenylcarbamate (XII) were converted into the *N*-phenyl derivatives of β-chlormethyl-μ-ketotetrahydrooxazole (IX) and α-chlormethyl-μ-



[1] This Journal, **44**, 352.

ketotetrahydrooxazole (X), or *β-chlormethyl-N-phenyl-μ-keto-tetrahydrooxazole* (XIII) and *α-chlormethyl-N-phenyl-μ-keto-tetrahydrooxazole* (XIV), respectively, when warmed with a strong solution of potassium hydroxide. It might be expected, therefore, that the corresponding acylurethanes (XV) and (XVI) would undergo analogous changes, in the presence of alkali, giving the corresponding tetrahydrooxazoles (IX) and (X), with formation of an aliphatic acid by hydrolysis. The acetyl- and benzoylurethanes of the haloid esters of glycerol were easily obtained by the action of acetyl- and benzoyl isocyanates[1] on these alcohols. These acyl cyanates, which have been little investigated, are far more reactive than phenyl isocyanate and the corresponding urethanes were all well-characterized, crystalline compounds. The benzoyl derivatives are more suitable for the identification of these glycerol haloid esters than the acetyl- or phenylurethanes because of their lesser solubility in the common organic solvents and their more characteristic melting points.

We now find that β,β′-dichlorisopropyl acetylcarbamate (XV) and the corresponding benzoylurethane are both changed, by the action of strong alkali, into a cyclic compound which is identical with the substance $C_4H_6O_2NCl$ obtained by Thomsen[2] by treatment of epichlorhydrin with potassium cyanate. Furthermore, these two acylurethanes condense like the phenylurethane examined by Johnson and Langley, and the cyclic compound is therefore assigned the structure of *α-chlormethylketotetrahydrooxazole*, as originally represented by Thomsen.[3] That it has not the structure of α-chlorpropyleneglyceryl imidocarbonate (V) is established by the following facts: It is soluble in alkali without decomposition, indicating the presence of a CO.NH grouping, and gives a monosilver salt. The compound apparently possesses no basic properties. A cyclic compound having the structure of an imidocarbonate (V) would be expected to possess properties similar to those of an acyclic imidocarbon-

[1] Billeter: Ber. d. chem. Ges., **36**, 3213.
[2] *Loc. cit.*
[3] *Loc. cit.*

ate, diethyl imidocarbonate, $HN:C(OC_2H_5)_2$,[1] and undergo hydrolysis, giving ammonia. Thomsen states that his compound underwent decomposition, with evolution of ammonia, when digested with dilute alkali. We are not able to confirm this statement, and obtained no evidence of the formation of any ammonia by digestion with an excess of a 20 per cent. solution of sodium hydroxide. It seems very probable to the writer that the ammonia detected by Thomsen resulted from a decomposition of a cyanate or some urea(?), which accompanied his tetrahydrooxazole as impurities.

The fact that β,β'-dichlorisopropyl acetyl- and benzoylcarbamates are converted into the same tetrahydrooxazole (IX) as is obtained by the action of potassium cyanate, in aqueous solution, on epichlorhydrin, shows that cyanic acid adds to this oxide in an analogous manner to the halogen acids, giving a secondary alcohol. *Therefore the NCO radical attaches itself to the carbon atom 3 at the end of the chain* $\overset{1}{C}.\overset{2}{C}.\overset{3}{C}$—. Whether this involves primarily an addition of H– and –OCN ions, giving a cyanic ester, and a subseqeunt rearrangement to an isocyanate, we have no evidence.

Attempts to prepare the isomeric α-chlormethyl-μ-ketotetrahydrooxazole (X) by the action of alkali on β,γ-dichlorpropyl and β-brom-γ-chlorpropyl acetylcarbamates were unsuccessful. The former urethane dissolved in cold alkali, without decomposition, giving a crystalline sodium salt, while the latter underwent hydrolysis under the same conditions, giving the urethane of β-brom-γ-chlorpropyl alcohol,

$$ClCH_2.CHBr.CH_2OCONH_2.$$

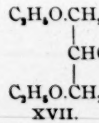
When heated with alkali, both urethanes underwent decomposition with formation of ammonia. In the case of the corresponding phenylurethanes[2] it was possible to change both forms into their corresponding oxazoles. However, it was observed that there was a remarkable difference in the ease with which these changes could be effected. The phenylurethanes of the α-dihalohydrins underwent the transformation

[1] Sandmeyer: Ber. d. chem. Ges., **19**, 864. Nef: Ann. Chem. (Liebig), **287**, 285. Hantzsch and Mai: Ber. d. chem. Ges., **28**, 2470.

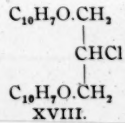
[2] Johnson and Langley: *Loc. cit.*

practically quantitatively at 50°–60°, while, on the other hand, the corresponding urethanes of the β-dihalohydrins (β-dichlorhydrin) showed lesser tendency to undergo cyclization under these conditions and were partly decomposed.

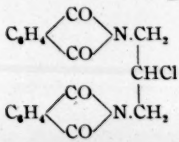
These results again illustrate, in a striking manner, the remarkable stability of secondary halides of the general formula $XCH_2CHCl.CH_2X$. Reboul and Lourenco,[1] who examined the action of sodium ethylate on α,γ-diethoxy-β-chlorpropane (XVII), write: "Durch eine concentrirte Lösung von Natriumalkoholat wird sie angegriffen, doch muss man zu Vervollständigung der Einwirkung das Gemische in einer zugeschmolzenen Rohre während einiger Stunden auf 120° erhitzen." The writer has also recently observed that α,γ-di-β-naphthoxy-β-chlorpropane (XVIII) and α,γ-diphthalimido-β-chlorpropane (XIX) can be digested with sodium ethylate for hours without removal of the halogen atom.



XVII.



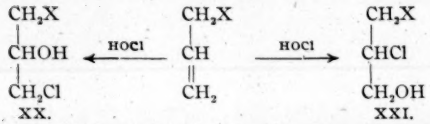
XVIII.



XIX.

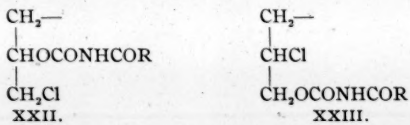
A simple method of determining easily the manner of addition of hypochlorous acid to allyl compounds is lacking. The common method is to subject the chlor alcohols obtained to oxidation[2] and ascertain by examination of the products of oxidation whether the original halohydrin was a secondary (XX) or a primary alcohol (XXI). In some cases, however,

[1] Ann. Chem. (Liebig). **119**, 238; Spl., **1**, 237.
[2] Ber. d. chem. Ges., **40**, 94.



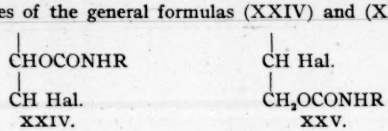
XX. XXI.

the hypochlorous acid adds in both ways, giving a mixture of alcohols which it is difficult to separate. The oxidation reactions also are oftentimes not smooth and consequently the products of the reaction are not formed in sufficient amount to purify and permit of identification with accuracy. Our observation of the remarkable difference in behavior, towards cold alkali, of acylurethanes of the types (XXII) and (XXIII) is therefore of especial interest.



XXII. XXIII.

It is the intention of the writer to continue the study of urethanes of the general formulas (XXIV) and (XXV):



XXIV. XXV.

EXPERIMENTAL PART.

β,β'-Dichlorisopropyl Acetylcarbamate, $\begin{matrix}CH_2Cl\\|\\CHOCONHCOCH_3\\|\\CH_2Cl\end{matrix}$.—Twelve grams of acetyl isocyanate, dissolved in dry ether, were added slowly to a cold ether solution of 18 grams of α-dichlorhydrin. There was an immediate reaction, with evolution of much heat, and in a few minutes a crystalline magma of the urethane was obtained. The yield was 28 grams, corresponding to 93 per cent. of the theo-

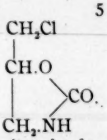
retical. It is soluble in benzene, hot water and alcohol. It was purified for analysis by crystallization from 95 per cent. alcohol and separated in clusters of needles melting at 100° to an oil. Analysis (Kjeldahl):

	Calculated for $C_4H_9O_2NCl_2$.	Found.
N	6.54	6.47

β,β'-Dichlorisopropyl Benzoylcarbamate, $\begin{matrix}CH_2Cl\\|\\CHOCONHCOC_6H_5\\|\\CH_2Cl\end{matrix}$.—This urethane was prepared like the preceding acetylcarbamate by the addition of 16 grams of benzoyl isocyanate to 16 grams of α-dichlorhydrin. It separated from the ether in colorless prisms which were purified by crystallization from alcohol. It crystallized in rectangular prisms which melted sharply at 119° to an oil. The compound is very soluble in benzene and insoluble in water. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NCl_2$.	Found.
N	5.07	5.02

β-Chlormethyl-μ-ketotetrahydrooxazole,



Preparation from β,β'-Dichlorisopropyl Acetylcarbamate.—Ten grams of potassium hydroxide were dissolved in 20 cc. of water and 5 grams of the acetylcarbamate addedin portions to the alkali solution. The urethane dissolved at once, with evolution of heat, and the solution gave a strong test for the chlorine ion. The excess of alkali was then neutralized with hydrochloric acid and the solution evaporated to dryness. The residue obtained was extracted with alcohol to remove the greater part of the potassium chloride and when the alcohol was evaporated we obtained the crude ketotetrahydrooxazole in crystalline form. It was purified by recrystallization from hot water and finally benzene. It separated from the lat-

ter solvent in prismatic crystals, which melted at 105°–106° to a clear oil. A mixture of this substance and of Thomsen's[1] compound (melting at 106°) melted at exactly the same temperature.

In a second experiment 5 grams of potassium hydroxide were dissolved in 20 cc. of water and 5 grams of the urethane added slowly to the solution as before. This dissolved immediately, and after allowing to stand for about 10 minutes, the alkaline solution was neutralized (cold) with hydrochloric acid. On standing, the oxazole separated in colorless prisms and after one crystallization from water melted at 106°. More of the compound was obtained from the filtrate in the manner described in the first experiment. Analysis:

	Calculated for $C_4H_6O_2NCl$.	Found.
Cl	26.63	26.30

Preparation from β,β'-Dichlorisopropyl Benzoylcarbamate.—Three-tenths gram of sodium was dissolved in absolute alcohol and 3.0 grams of the carbamate added at once to the solution. There was an immediate reaction, with separation of sodium chloride, and with evolution of sufficient heat to cause the solution to boil. After heating about 10–15 minutes, on the steam bath, the sodium chloride was filtered off and the alcohol filtrate concentrated. We obtained an oil which was insoluble in cold water and having a strong odor of ethyl benzoate. It was dissolved in ether to remove inorganic salts and when the solution was allowed to evaporate spontaneously we obtained a crop of prisms suspended in ethyl benzoate. They melted at 105°–106°, without further purification, and were identified as *β-chlormethyl-μ-ketotetrahydrooxazole*. When the oil was digested with alkali it dissolved, and on addition of hydrochloric acid to the alkaline solution benzoic acid melting at 120° separated. The yield of oxazole obtained from the benzoylcarbamate was small. Analysis (Kjeldahl):

	Calculated for $C_4H_6O_2NCl$.	Found.
N	10.3	10.0

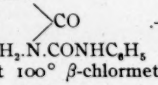
[1] *Loc. cit.*

Digestion of β-Chlormethylketotetrahydrooxazole with Alkali.—About 0.1 gram of the oxazole was dissolved in 350 cc. of 20 per cent. sodium hydroxide and the solution subjected to a Kjeldahl distillation, the distillate being passed into 10 cc. of 0.1 N hydrochloric acid. After distilling over about one-half the liquid, 9.85 cc. of a 0.1 N sodium hydroxide solution, were required to neutralize the free hydrochloric acid present.

Silver Salt of β-Chlormethylketotetrahydrooxazole.—This separated as a white, gelatinous precipitate when the calculated quantity of silver nitrate was added to an aqueous solution of the sodium salt of the ketotetrahydrooxazole. After washing with water and alcohol it was dried for analysis in a desiccator over concentrated sulphuric acid.

	Calculated for $C_4H_5O_2NClAg$.	Found.
A	44.54	46.0

β-Chlormethylketotetrahydrooxazylphenylurea,

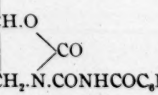


.—This urea was prepared by warming at 100° β-chlormethylketotetrahydroxazole, prepared by our method and also by Thomsen's, with a molecular proportion of phenyl isocyanate. It crystallized from alcohol in rhombic tables melting at 154°–155° to an oil without effervescence. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3N_2Cl$.	Found.
N	11.00	10.60

β-Chlormethylketotetrahydrooxazole was recovered unaltered after heating with phenyl isothiocyanate at 100° for 3 days.

β-Chlormethylketotetrahydrooxazylbenzoylurea,



.—A quantitative yield of this urea was

obtained by warming 0.8 gram of the tetrahydrooxazole with 0.9 gram of benzoyl isocyanate for a few minutes at 100°. It crystallizes from 95 per cent. alcohol in rhombic prisms, which melt at 131°–132° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{11}O_4N_2Cl$.	Found.
N	9.9	9.55

β,γ-Dichlorpropyl Acetylcarbamate, $CH_2Cl \cdot CHCl \cdot CH_2OCONHCOCH_3$.—Acetyl isocyanate reacts immediately with β,γ-dichlorpropyl alcohol in ether, giving a quantitative yield of this urethane. When the ether was allowed to evaporate spontaneously it deposited in colorless prisms which were very soluble in benzene, alcohol and acetone, but insoluble in ligroin. It was purified by crystallization from benzene and separated in well-developed prisms melting at 64°–65° to an oil. Analysis (Kjeldahl):

	Calculated for $C_6H_9O_3NCl_2$.	Found.
N	6.55	6.60

Action of Alkali on β,γ-Dichlorpropyl Acetylcabamate.—Three and five-tenths grams of this urethane were added to 15 cc. of a cold aqueous solution of potash, prepared by dissolving 1 part of the alkali in 4 parts of water. It dissolved at once and then suddenly a sodium salt separated in the form of glistening plates. These were filtered off and dissolved in water and hydrochloric acid added cautiously to the solution when an oil separated which soon crystallized. The substance was very soluble in alcohol, benzene, and insoluble in ligroin. After purification by crystallization from benzene it melted at 64°–65° and was identified as the unaltered β,γ-dichlorpropyl acetylcarbamate. Analysis (Kjeldahl):

	Calculated for $C_6H_9O_3NCl_2$.	Found.
N	6.55	6.50

Allyl Acetylcarbamate, $CH_2:CH \cdot CH_2O \cdot CO \cdot NHCOCH_3$.—

This was prepared by the action of acetyl isocyanate on allyl alcohol in ether solution. It is very soluble in benzene, ethyl alcohol and chloroform. It was purified by crystallization from a mixture of benzene and ligroin and separated in long, flat prisms melting at 64° to an oil. Analysis (Kjeldahl):

	Calculated for $C_6H_9O_3N$.	Found.
N	9.86	9.80

β-Brom-γ-chlorpropyl Acetylcarbamate,

$$\begin{array}{l} CH_2Cl \\ | \\ CHBr \\ | \\ CH_2OCONHCOCH_3 \end{array}$$

.—Four grams of β-brom-γ-chlorpropyl alcohol and 2 grams of acetyl isocyanate were dissolved in ether and the solution allowed to evaporate spontaneously. The urethane separated as an oil. This finally solidified on standing and was purified for analysis by dissolving in benzene and precipitating from this solvent with ligroin. It separated as an oil, which soon crystallized in prisms, melting at 60° to an oil. The urethane is very soluble in alcohol and benzene. Analysis (Kjeldahl):

	Calculated for $C_6H_9O_3NClBr$.	Found.
N	5.34	5.42

Action of Alkali on β-Brom-γ-chlorpropyl Acetylcarbamate.—Eight grams of potassium hydroxide were dissolved in 32 cc. of water and 8 grams of the carbamate added to the cold solution. It dissolved immediately on stirring and in a few minutes a colorless crystalline substance separated. This was insoluble in cold water and very soluble in alcohol, but crystallized from dilute alcohol in plates melting at 93°. The compound contained chlorine and bromine and when warmed with alkali, it was decomposed with evolution of ammonia. A nitrogen determination indicated that it was *β-brom-γ-chlorpropyl carbamate,*

$$\begin{array}{l} CH_2Cl \\ | \\ CHBr \\ | \\ CH_2OCONH_2 \end{array}$$

	Calculated for $C_4H_7O_2NClBr$.	Found.
N	6.47	6.32

The following urethanes were all prepared by dissolving the corresponding alcohols in ether and then adding the calculated quantity of benzoyl isocyanate diluted with ether. In some cases the urethanes separated in crystalline form in a short time, but in others they were very soluble and were obtained, after spontaneous evaporation of the ether, as oils which soon crystallized on standing.

β,β'-Dibromisopropyl Benzoylcarbamate, $(BrCH_2)_2CHOCONHCOC_6H_5$.—From α-dibromhydrin and benzoyl isocyanate. It is very soluble in benzene and crystallizes from alcohol in plates melting at 119°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NBr_2$.	Found.
N	3.84	3.83

β,β'-Chlorbromisopropyl Benzoylcarbamate,

$$\begin{array}{l} CH_2Br \\ | \\ CHOCONHCOC_6H_5 \\ | \\ CH_2Cl \end{array}$$

—From α-chlorbromhydrin and benzoyl isocyanate. It separated from the ether in colorless crystals and crystallized from alcohol in long needles melting at 122°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NClBr$.	Found.
N	4.37	4.18

β,γ-Dichlorpropyl Benzoylcarbamate, $ClCH_2.CHCl.CH_2OCONHCOC_6H_5$.—This was obtained as an oil, after evaporation of the ether, which finally crystallized on standing. It is very soluble in alcohol, benzene and acetone. It was purified by crystallization from a mixture of benzene and ligroin and melted at 83°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_2NCl_2$.	Found.
N	5.07	5.30

β,γ-Dibrompropyl Benzoylcarbamate,

$BrCH_2CHBr.CH_2OCONHCOC_6H_5$.—This urethane is very soluble in alcohol, ether and benzene. It was purified by crystallization from a mixture of benzene and ligroin and melted at 83° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_2NBr_2$.	Found.
N	3.83	3.78

β-Brom-γ-chlorpropyl Benzoylcarbamate,

$ClCH_2CHBr.CH_2OCONHCOC_6H_5$.—This is very soluble in ether, benzene and alcohol. It crystallized from cold ethyl and methyl alcohols in tabular crystals melting at 113°. A mixture of this compound and of *β,β'*-chlorbromisopropyl benzoylcarbamate (melting at 122°) melted at 110°–115°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_2NClBr$.	Found.
N	4.37	4.25

β-Chlor-γ-brompropyl Benzoylcarbamate,

$BrCH_2CHCl.CH_2OCONHCOC_6H_5$.—This urethane was obtained as an oil which crystallized on long standing. It is very soluble in all the common organic solvents except ligroin. It was purified by crystallization from alcohol and separated in prisms melting at 114°. A mixture of this urethane and of *β,β'*-dichlorisopropyl benzoylcarbamate melted at 110°–116°. A mixture of the urethane and of the isomeric *β*-brom-*γ*-chlorpropyl benzoylcarbamate melted at 113°–114°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_2NClBr$.	Found.
N	4.37	4.50

NEW HAVEN, CONN.,
June 15, 1910.

THE PRECIPITATION OF VANADIC ACID AS SILVER VANADATE, AND THE ESTIMATION OF PHOSPHORIC AND VANADIC ACIDS IN THE PRESENCE OF ONE ANOTHER.

By Graham Edgar.

I. The Precipitation of Vanadic Acid as Silver Vanadate.

Three salts of silver and vanadic acid have been described by Ditte[1] and others, the dark red orthovanadate, Ag_3VO_4, the dark yellow crystalline pyrovanadate, $Ag_4V_2O_7$, and the pale yellow metavanadate, $AgVO_3$. All of these are insoluble in water and dilute acetic acid, and soluble in ammonium hydroxide and nitric acid. They may be readily obtained by the action of silver nitrate upon fresh solutions of the corresponding alkali salts, but unless special precautions are taken mixtures of the various salts are always formed. The writer has thought it desirable to study the character of the precipitate formed by silver nitrate and solutions of alkali vanadate under various conditions, with the object of finding conditions under which a precipitate of constant composition is formed, thus permitting the quantitative estimation of vanadic acid as silver salt, either gravimetrically, or volumetrically by an adaptation of the well-known Volhard method for the estimation of silver.

In all of the experiments described below the same general plan was followed; a known quantity of standard solution of sodium vanadate was treated with an excess of 0.1 N silver nitrate, and the excess of silver was determined in the filtrate from the precipitated silver vanadate by titration with standard ammonium thiocyanate. The composition of the precipitate was then calculated from the amount of silver used, qualitative tests having shown that the filtrate contained no vanadium.

In Table (I*a*) are given the results of experiments made on a solution of pure sodium pyrovanadate. The method of treatment was as follows: To measured portions of the solu-

[1] Compt. rend., **104**, 1705.

tion a considerable excess of 0.1 N silver nitrate was added, the precipitate was dissolved in the least possible quantity of ammonium hydroxide, and the solution was boiled until the odor of ammonia had disappeared. The flask was then cooled and allowed to stand for a few minutes. Under these conditions a dark red precipitate was obtained which settled readily, leaving a colorless solution. The solution was filtered through asbestos on a perforated crucible, and the filtrate was titrated with ammonium thiocyanate, after the addition of nitric acid and ferric nitrate. The results show that under these conditions the vanadic acid is quantitatively precipitated as silver orthovanadate, Ag_3VO_4, and that in a solution of pure sodium pyrovanadate, the vanadium may be very simply estimated in this manner:

Table Ia.

V_2O_5 taken. Gram.	0.1 N $AgNO_3$ required. cc.	V_2O_5 found. Gram.	Error V_2O_5. Gram.	Remarks.
0.1183	38.94	0.1184	+0.0001	Calculated as
0.1183	38.88	0.1182	—0.0001	Ag_3VO_4
0.0503	16.58	0.0504	+0.0001	
0.0887	29.18	0.0887	±0.0000	
0.0887	29.18	0.0887	±0.0000	
0.0591	19.37	0.0589	—0.0002	
0.0591	19.44	0.0591	±0.0000	

Table Ib.

0.0887	19.41	0.0885	—0.0002	Calculated as
0.0887	19.39	0.0884	—0.0003	$Ag_4V_2O_7$
0.0887	19.39	0.0884	—0.0003	Acidified with
0.0591	12.89	0.0587	—0.0004	acetic acid
0.0591	12.90	0.0588	—0.0003	
0.0591	12.95	0.0590	—0.0001	Acidified with
0.0887	19.41	0.0885	—0.0002	nitric acid
0.0887	19.41	0.0885	—0.0002	

In Table *Ib* are given the results of experiments in which the solution of sodium pyrovanadate was acidified with acetic or nitric acid, before the addition of the silver nitrate. Ammonium hydroxide was then added, and the determinations carried out as before. The results show that under these

conditions the pyrovanadate, $Ag_4V_2O_7$, is precipitated, the results being nearly quantitative, though a little low in every case. In this process, however, great difficulty was experienced in preventing the violent bumping of the solution during the boiling off of the ammonia, fragments of porous tile being entirely inadequate to prevent this.

Either of the above methods would give satisfactory results for the estimation of vanadium in a solution of pure sodium vanadate, but it is obvious that to be of practical use a method must be applicable to the solutions of vanadium obtained in the ordinary course of analysis, which usually are either acid or else contain an indefinite amount of alkali. Accordingly a solution of sodium vanadate was prepared by boiling barium vanadate with an excess of sodium carbonate, and filtering from the barium carbonate. This solution was used in all the work described below.

Experiments showed that if such a solution is acidified with nitric acid, boiled to expel the carbon dioxide, and then neutralized with calcium carbonate, direct precipitat on with silver nitrate gives a precipitate of varying composition, consisting largely of the pyrovanadate. If this precipitate is dissolved in ammonium hydroxide and reprecipitated by boiling off the ammonia, the orthovanadate is formed, but the calcium carbonate reacts to some extent with the silver nitrate, causing uncertain results.

The plan was then tried of acidifying the vanadate solution with nitric acid, boiling off the carbon dioxide as before, and then adding dilute sodium hydroxide to the boiling solution until the yellow color had disappeared. Under these conditions the solution is only faintly alkaline to phenolphthalein, and direct precipitation with silver nitrate gives the metavanadate, $AgVO_3$, the composition of the precipitate, however, varying considerably. If ammonium hydroxide is added and the excess of ammonia removed by boiling, the orthovanadate, Ag_3VO_4, is precipitated, and excellent results may be obtained for the estimation of vanadium. Table II gives some results obtained in this manner. The following directions may, therefore, be given for the estimation of vana-

Table II.

V_2O_5 taken. Gram.	0.1 N $AgNO_3$. cc.	V_2O_5 found. Gram.	Error. Gram.
0.1257	41.32	0.1256	—0.0001
0.1257	41.40	0.1258	+0.0001
0.1257	41.35	0.1257	±0.0000
0.0628	20.60	0.0626	—0.0002
0.0628	20.66	0.0628	±0.0000
0.1885	62.00	0.1885	±0.0000
0.1885	62.04	0.1886	+0.0001
0.1257	41.33	0.1256	—0.0001

dium in solutions of alkali vanadate containing an excess of carbonate but no other substance precipitated by silver nitrate in neutral or ammoniacal solution:

The solution is acidified with nitric acid and boiled to expel the carbon dioxide. A yellow color, at first deep and then fading somewhat, is formed by this treatment. Dilute sodium hydroxide is then added to the boiling solution until the color changes back through deep yellow to colorless. An excess of standard silver nitrate solution is then added, the precipitate is dissolved in ammonium hydroxide, and the solution boiled until the odor of ammonia has disappeared. A few fragments of porous tile are added to prevent bumping. The solution is cooled and filtered through asbestos (or paper) and the filtrate is acidified with nitric acid and titrated with standard ammonium thiocyanate. The vanadic acid is calculated on the assumption that the precipitate is the orthovanadate, Ag_3VO_4 (one cc. of 0.1 N $AgNO_3$ is equivalent to 0.00304 gram of V_2O_5). An advantage of this method lies in the smallness of this factor, it being only one-third of that for 0.1 N solutions in the oxidimetric process.

II. The Estimation of Phosphoric and Vanadic Acids in the Presence of One Another.

Many methods for the separation of phosphoric and vanadic acids have been devised, but none of them are altogether satisfactory. Perhaps the best is that of Holverscheit,[1] in

[1] Diss., Berlin, 1890.

which the phosphoric acid is precipitated by molybdic solution after the reduction of the vanadic acid with sulphur dioxide. This method is accurate, but leaves the vanadium in an unsatisfactory condition for further work.

The use of combined volumetric processes for the estimation of vanadium and other elements in the presence of one another has proved so successful in other instances[1] that it has seemed to the writer that in this case also the separation of phosphoric and vanadic acids might be avoided, and the two estimated in the same solution by precipitation as silver salts. Silver nitrate gives with neutral or slightly alkaline solutions of sodium phosphate a precipitate of yellow silver phosphate, Ag_3PO_4, and if this precipitate is dissolved in ammonium hydroxide, and the excess of ammonia removed by boiling, the phosphoric acid may be estimated volumetrically by the titration of the excess of silver nitrate in the filtrate from the silver phosphate. It is obvious that if vanadic and phosphoric acids were present in the same solution this process would determine the sum of both acids, and if the vanadium were estimated in the precipitate, the phosphoric acid could be determined by difference. Table III gives the results of experiments on solutions containing sodium phosphate and vanadate in varying amounts, together with an excess of sodium carbonate. The technique was exactly the same as that given above for the estimation of vanadium, with the exception that the precipitate of silver vanadate and phosphate was washed back from the filter into the flask in which precipitation was made, and the vanadium was determined by solution in sulphuric acid, reduction with sulphur dioxide, and titration of the hot solution with 0.05 N potassium permanganate, after removing the excess of sulphur dioxide by boiling, a current of carbon dioxide being passed through the solution. The phosphoric acid was then determined by difference (one cc. of 0.05 N $KMnO_4$ is equivalent to 0.00456 gram of V_2O_5, and one cc. of 0.1 N $AgNO_3$ to 0.00304 gram V_2O_5 or 0.0023667 gram of P_2O_5).

[1] Am. J. Sci., **25**, 332; **26**, 79, 333; **27**, 174, 299. J. Ind. Eng. Chem., **1**, 661.

Table III.

V_2O_5 taken. Gram.	P_2O_5 taken. Gram.	0.1 N $AgNO_3$ required. cc.	0.05 N $KMnO_4$ required. cc.	V_2O_5 found. Gram.	Error V_2O_5. Gram.	P_2O_5 found. Gram.	Error P_2O_5. Gram.
0.1257	0.0331	55.31	27.70	0.1258	—0.0001	0.0329	—0.0002
0.1257	0.0331	55.26	27.68	0.1257	±0.0000	0.0329	—0.0002
0.1257	0.0662	69.26	27.64	0.1255	—0.0002	0.0662	±0.0000
0.0628	0.0662	48.56	13.82	0.0627	+0.0001	0.0661	—0.0001
0.0628	0.0662	48.55	13.84	0.0628	±0.0000	0.0660	—0.0002
0.0628	0.0996	62.50	13.84	0.0628	±0.0000	0.0995	—0.0001
0.1257	0.0996	83.26	27.70	0.1258	+0.0001	0.0994	—0.0002
0.1885	0.0331	75.92	41.50	0.1884	—0.0001	0.0330	—0.0001
0.1885	0.0331	75.95	41.58	0.1888	+0.0003	0.0328	—0.0003
....	0.0331	13.95	...	....	.....	0.0330	—0.0001
....	0.0662	27.85	...	....	.....	0.0659	—0.0003
....	0.0996	41.92	...	....	.....	0.0995	—0.0001

SUMMARY.

Conditions have been found under which vanadic acid may be quantitatively precipitated as silver orthovanadate, and a process for the estimation of vanadic acid, based on this fact, has been devised.

Phosphoric and vanadic acids may be estimated volumetrically in the presence of one another by precipitation as silver salts under the conditions described above, the vanadium being determined oxidimetrically in the precipitate, and the phosphoric acid by difference.[1]

UNIVERSITY OF VIRGINIA.
July, 1910.

OBITUARIES.

HENRY AUGUSTUS TORREY.

August 29, 1871–March 25, 1910.

Henry Augustus Torrey was a professor by right of birth, as his father was H. A. P. Torrey, professor of philosophy in the University of Vermont, and his maternal grandfather was President Torrey of the same institution. After graduating at Burlington, he took the degree of Doctor of Philosophy in

[1] NOTE.—Since the above work was done a paper by Browning and Palmer has appeared in the Am. J. Sci., Sept., 1910, describing a method by which vanadium may be estimated by precipitation as silver metavanadate, the precipitate being ignited and weighed as $AgVO_3$.

Chemistry at Harvard University, and continued his studies for a year in Leipzig and Berlin, returning to teach in the University of Vermont from 1898 to 1903, when he was called to Harvard University, and there he remained as instructor and later assistant professor of organic chemistry till the time of his death.

Of his more important investigations, that on the complex phenols, which are insoluble in alkalies, should undoubtedly come first. In this he showed himself a master of the art of testing working hypotheses by well-conceived experiments, and collected so many observations that a firm basis has been secured for the solution of this difficult problem. Next I should place his discovery and thorough study of iodanil, perhaps because my own unsuccessful attempts to make iodorthoquinones have impressed me with the difficulty of such work; but it may be that the second place should be given to his work on pyromucylacetic ester, which furnished another member of the acetacetic ester family, and led to the discovery of new pyrazolones.

Other interesting researches are his study of the complicated reaction of paranitrosodialkylanilines with ethylene dibromide, and of the isomeric red and white silver salts of tribromphenol. His work on the last subject was restricted to a brief excursion into this field to avoid interference with Hantzsch, but even in this he succeeded in throwing much light on these obscure phenomena. His proof that phenoquinone, or quinhydrone, is entirely dissociated when in solution is perhaps the best but not by any means the only example of his fruitful application of physico-chemical methods to organic work.

Without enumerating the subjects of his other papers, enough has been said to show the high quality of his work. The quantity also is considerable, as his chemical activity will be represented by over twenty-five papers, when all his work has been published. With the exception of very few, these date from his less than seven years of service in Cambridge, where the burden of teaching was lightened enough to allow him time for research; and this large production becomes the more remarkable when it is known that for the last twenty years of his life he was suffering from a disability, under which almost any other man would have sunk into a hopeless invalid; but with him it interfered with no duty, and was borne in such heroic silence that his most intimate colleagues knew nothing of its existence, until after it had killed him.

In addition to his capacity for original work, he possessed exceptional ability as a teacher, which thronged his classes in organic chemistry with eager and enthusiastic students.

The loss of his retiring but most attractive personality brings a keen sorrow to his colleagues and friends, and all chemists must grieve that the Science has been deprived of the brilliant future foretold by what he had already accomplished.

C. LORING JACKSON.

HUGO ERDMANN.

Professor Hugo Erdmann, of Berlin, Germany, who was drowned while yachting on June 25th, was born in East Prussia in 1862, and was therefore 48 years old at the time of his death.

Graduating from the Gymnasium at Tilsit, Erdmann studied in the universities of Halle, Munich and Strassburg. In 1883 he was chosen as assistant to Volhard in the Halle laboratory; in 1885 he became Privat-dozent, and in 1894 professor. In 1901 he was called to Berlin as Professor of Inorganic Chemistry and Director of the Laboratory in the Royal Institute of Technology at Charlottenburg.

His first scientific work was a share in the investigations of his teacher, Fittig, at Strassburg, on the unsaturated acids; in the course of these researches he accomplished the synthesis of α-naphthol from phenylisocrotonic acid. His work in the earlier years of his stay in Halle was in both inorganic and organic chemistry, and his books, "Anleitung zur Darstellung chemischer Präparate" (inorganic), published in 1891, and "Anleitung zur Darstellung organischer Präparate," published in 1894, made his name familiar to students.

The publication of the first of these books brought about a change in the laboratory methods of teaching inorganic chemistry. Many teachers in this country, in England and in Germany, use either Erdmann's book or one of its many successors, thus returning from the method of laboratory instruction by analysis only to the use of both analysis and preparations which was the method of Wöhler. We should not forget that Erdmann was the leader of this movement.

Erdmann's "Lehrbuch der anorganischen Chemie," published in 1898, met with a reception so favorable that a fourth edition appeared in 1906. This book is his greatest achievement; it stands in a class by itself; it is a descriptive textbook unrivaled and unapproached in its combined accuracy, completeness and compactness.

Collaborating with Köthner, he published, in 1905, a book on the "Constants of Nature."

His later experimental work was mostly in the inorganic field. He was much interested in the gases of the atmosphere and devised an improved apparatus for isolating argon. He gave much time to the study of liquid air and the accurate separation of its constituents; starting from the fact that solid nitrogen melts 20° higher than solid oxygen, he devised apparatus in which all of the nitrogen in a vessel of liquid air is frozen while all of the oxygen remains liquid, pure nitrogen and pure oxygen being obtained by filtration. The importance of pure nitrogen in making calcium cyanamide led him to patent this process.

Among his later articles is his work on thiozonides, or organic derivatives of the active form of sulphur S_3, corresponding to ozone.

Through the death of Erdmann, cut off in the fulness of his activity, inorganic chemistry has lost an energetic and productive worker. E. R.

CHARLES ANTHONY GOESSMANN.

Charles Anthony Goessmann, Ph.D., LL.D., Honorary Professor of Chemistry in the Massachusetts Agricultural College, and Honorary Director of the Massachusetts Agricultural Experiment Station, died at his home in Amherst, Mass., on September 1, 1910, at the age of 83.

Dr. Goessmann was born in Naumburg-Hesse, Germany, June 13, 1827. He was a student of Wöhler, under whom he took his doctor's degree at Göttingen in 1852, and it was due to this master's influence that he gave up his plan of becoming a pharmacist and took up the work of pure chemistry. He remained at Göttingen until 1857 as Wöhler's assistant, and it was during this time that he met the two Americans who were instrumental in bringing him to this country.

The Eastwick Bros. owned sugar plantations in Cuba and at their request Dr. Goessmann came to Philadelphia in 1857 as chemist and manager of their sugar company. He remained in this position until 1860, when he resigned and spent several months in Cuba, studying the production of sugar cane on the plantations there. In April, 1861, he entered the employ of the Onandaga Salt Co., of Syracuse, N. Y., where he remained until 1869. From 1861–1864 he was Professor of Chemistry and Physics in the Rensselaer Polytechnic Institute. In 1869, at the invitation of another of his Göttingen friends, President W. S. Clark, of the Massachusetts Agricultural College, he accepted the chair of Chemistry in this newly established institution. In either active or honorary service he held this position for a period of 41 years, until his death.

While professor of Chemistry in the college, he held simultaneously the positions of chemist to the Massachusetts State Board of Agriculture and State Inspector of Fertilizers, and analyst to the State Board of Health. In 1882, when the Massachusetts State Experiment Station was established, he became director and chemist, a position which he held until his retirement in 1907. He was a member of various scientific societies and commissions, being president of the American Chemical Society in 1887. He was one of the founders and was first president of the Association of Official Agricultural Chemists. In 1889 Amherst College gave him the degree of LL.D. In 1907 the trustees of the Carnegie Foundation granted him a pension and he retired from active service.

Coming to this country, as he did, just at the time when the idea of agricultural colleges and experiment stations was developing, it was only natural that a chemist, with a taste for the practical applications of his science, should have found inviting opportunities for taking part in the establishment and shaping of such institutions. He took a leading part in the shaping of the policies of our agricultural experiment stations, and this was especially true in connection with the questions of fertilizers and fertilizer control. It was largely through his influence and labor that the first Massachusetts state law for the control of fertilizer manufacture was passed and he naturally became chemist in charge of the inspection and analysis. This was pioneer work in this field, but the ideas and policies he advocated have since been adopted in practically all laws which have to do with fertilizer control.

His own tastes, his work with Wöhler, the inspiration of Liebig's views on the relation of chemistry to agriculture, his brief connection with sugar refining and the sugar plantations of Cuba and his call to the chair of Chemistry in one of the new agricultural colleges, all led him into the agricultural side of his science. His more important contributions to Chemistry, which number about two hundred, are therefore chiefly along the lines of investigations in pure and practical agriculture, such as sugar and sugar cane, soils, plant composition and plant nutrition, fertilizers, animal feeding, etc. His researches on plant composition and plant nutrition and on animal feeding—lines of work for which the experiment station of which he was so long director and chemist, has become so well known—are perhaps his greatest contribution to agricultural chemistry. During his stay at Göttingen, however, he published some twenty-five papers in organic chemistry

on the constituents of Cantharides, The Production of Leucine from Thialdin, The Constitution of Leucine, Arachidic Acid, etc., and while connected with the salt works at Syracuse he visited and investigated the salt deposits in Michigan, Louisiana and Canada, in addition to those of Onandaga Co., N. Y., publishing reports of these investigations.

As Professor of Chemistry in the Massachusetts Agricultural College, Dr. Goessmann was one of those instructors who won the universal esteem of his students. This esteem and the inspiration he gave to all his pupils was founded not only on his gentleness and friendliness as a man, qualities which endeared him to everyone, but also on his integrity and industry as a scientist. His example was that of both the investigator and the teacher. The work he did showed the man he was and his students believed in him and loved him. They saw in him a chemist who was accurate, industrious and practical, a worker who was painstaking and who never hurried, a teacher and man who was friendly and helpful.

On three occasions Professor Goessmann was the recipient of tokens of his students' regard and affection. On his eightieth birthday the Alumni of the Massachusetts Agricultural College presented him with a stained-glass window, symbolic of his life and work, which hangs in the study of his home. At the last Commencement, in June, 1910, the same body presented to their Alma Mater a portrait of their honored teacher, to be hung on the college walls together with those of the other founders of the institution. The last occasion was on October 12th, when the Massachusetts Agricultural College held a memorial service in honor of the man who had recently passed away. At this time Kenyon L. Butterfield, LL.D., President of the institution, Professor Charles Wellington, Dr. Goessmann's successor in the chair of Chemistry in the College, Professor Charles F. Chandler of Columbia University, a fellow student in Göttingen, and President W. E. Stone, of Purdue University, a pupil and coworker, paid loving and honored tribute to the man and the scientist.

JOSEPH H. CHAMBERLAIN.

REVIEWS.

ABHANDLUNG ÜBER DIE GLYKOLE ODER ZWEIATOMIGE ALKOHOLE UND ÜBER DAS AETHYLENOXYD ALS BINDEGLIED ZWISCHEN ORGANISCHER UND MINERALCHEMIE. Von ADOLF WURTZ. OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN, No. 170. Leipzig: Wilhelm Engelmann. 1909. pp. 96. Price, M. 1.80.

These famous articles have been translated and annotated

by M. and A. Ladenburg. The first appeared originally in 1859, the second in 1862. The translators say in regard to them that they belong to the most important by the author, who is one of the greatest chemists of France.

There can be no doubt that these articles strongly influenced the thoughts of chemists and were of great aid in giving clear conceptions of the atomicity of radicals. The difference between the monatomic radical, C_2H_5, the diatomic radical, C_2H_4, and the triatomic radical, C_3H_5, of glycerol, was for the first time brought out, and the recognition of these differences led in turn to the recognition of similar differences between the elements. All this paved the way for the views in regard to constitution put forward a little later by Couper and Kekulé—views that still prevail, although over forty years have elapsed since they were first presented. I. R.

THE OXIDASES AND OTHER OXYGEN CATALYSTS CONCERNED IN BIOLOGICAL OXIDATIONS. By J. H. KASTLE. Hygienic Laboratory, Public Health and Marine Hospital Service of the United States. Bulletin No. 59, December, 1909. Washington: Government Printing Office. 1910. pp. 164.

This bulletin contains an interesting résumé of the literature of the oxidases written by Professor Kastle, who has himself made important contributions to our present knowledge of this intricate subject. The work is divided into three sections. The first contains an excellent account of the historical development of the different theories of oxidation in which the author has incorporated much interesting information of a chemical character not directly connected with the tissue-oxidases. In this way the scope of the essay is advantageously broadened.

The second part is devoted to a more or less detailed account of the oxidizing ferments, while the last section is devoted to the Catalases and Peroxidases.

The work as a whole must be regarded as a very helpful contribution to the literature of a difficult subject. At the same time it appears to the reviewer to be a matter for regret that while many of the less important oxidizing reactions of the tissues are referred to in some detail, the question of the oxidation of the physiologically important substances present in the animal body—especially the amino acids, carbohydrates and fats—is very largely ignored.

A bibliography containing 467 references is a valuable feature. H. D. DAKIN.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. A Treatise on the Properties, Modes of Assaying, and Proximate Analytical Examination of the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicines, etc., with Concise Methods for the Detection and Estimation of their Impurities, Adulterations and Products of Decomposition. Volume I.—Introduction, Alcohols, Yeast, Malt Liquors and Malt, Wines and Spirits, Neutral Alcoholic Derivatives, Sugars, Starch and Its Isomerides, Paper and Paper-making Materials, Vegetable Acids. By the Editors and the Following Contributors: E. F. ARMSTRONG, J. L. BAKER, G. C. JONES, E. SCHLICHTING and R. W. SINDALL. Fourth edition, entirely rewritten. Edited by HENRY LEFFMANN, M.A., M.D., Professor of Chemistry and Toxicology in the Woman's Medical College of Pennsylvania, and in the Wagner Free Institute of Science, Philadelphia, and W. A. DAVIS, B.Sc., A.C.G.I., formerly Lecturer and Assistant in the Chemical Research Laboratory, City and Guilds College, Imperial College of Science and Technology, London. Philadelphia: Blakiston's Son & Co. 1909 pp. x + 576. Price, $5.00.

Volume I of the fourth edition of Allen's Commercial Organic Analysis has been awaited with interest because of the standard nature of the work and because the field covered is being so rapidly extended; that this edition has followed the last so closely indicates the deserved popularity of the book.

The plan followed in the present volume has been to allot the various subjects treated to specialists; the book has been largely rewritten and has been increased in size to the extent of 20 pages. The chapter on "Alcohols" of previous editions has been divided into "Alcohols," "Malt and Malt Liquors," and "Wines and Potable Spirts." New articles on "Yeast" and "Paper and Paper-making Materials" are included. The scope of the book is therefore considerably broadened.

Inasmuch as it is stated in the preface that "By the selection of contributors from both sides of the Atlantic the work has been made more distinctly international.....," it is somewhat surprising that saccharimeters, which are used so extensively in this country, particularly in commercial work, are given but a half-page description.

Cereals other than wheat also receive very scanty treatment; the factor 6.33 is given for the calculation of protein from nitrogen in cereals. The estimation of sugars by means of the refractometer does not mention Geerlig's or other recent work in this field. On page 290, in referring to the solution densities of carbohydrates, it is stated that the "sum of the carbohydrates present in an aqueous solution may be found approximately by allowing an increase of 3.86 in density for each one gram of carbohydrate in 100 cc. of the liquid. This figure is correct for very dilute solutions....." This figure is recognized as correct only for solutions of an approximate concentration of ten grams per 100 cc.

In the discussion of the determination of volatile acids in wines the Sellier apparatus, as recommended by Hortvet, which appears to be of great value, is not mentioned. The hydrochloric acid-iron test for formaldehyde is stated to produce a "red" color, which would be misleading to one unfamiliar with the color produced.

On page 358 is found the sentence " . . . in accordance with the provisions of the U. S. (Federal) food law the following *eight* colors are permitted, . . ." which is apparently a typographical error. "Laeonlose," on page 401, should be *levulose*. On page 497 is the statement that "Cider vinegar is *yellowish*, has an odor of apples, a sp. gr. of *1.013 to 0.115*," which obviously is not an accurate description of this product. From "1.5 to 1.8 per cent. of extract" would seem to be a narrow margin inasmuch as the standard in a number of the states is that cider vinegar should not contain less than 2 per cent. of extractive matter. It is also stated that cider vinegar *always* gives a precipitate with lead acetate, which is not true of certain abnormal cider vinegars.

The chapter on "Paper and Paper-making Materials" is by R. W. Sindall. The usual physical, chemical and microscopical methods are stated in a general and brief way, so briefly indeed that it is doubtful if this chapter will prove very helpful either to the experienced paper analyst or to the uninitiated. Cautionary remarks regarding the accuracy of results which can be obtained by some of the methods given would have been quite helpful. Thus it is well known that the usual methods for the quantitative determination of starch give very inaccurate results on many classes of paper, so inaccurate indeed that in many instances they are not even approximations.

The methods for the quantitative determination of rosin and for the detection of free acids in paper would seem to need amplification. The same criticism can be made of the method given for the determination of the percentage of various kinds of fiber. A statement covering the maximum, minimum, and average size of the various fibers would have been helpful. There are included microphotographs of the more common paper-making fibers.

Because of the detail of these criticisms the work should not be judged harshly, as a majority of the suggestions do not reflect upon the book as a whole, which is a valuable treatise, as have been the earlier editions, but refer rather to surface faults. The new plan followed in this edition, in which each chapter is written by a specialist, seems particularly worthy

of commendation; uniformity is apparent in weights and measures, nomenclature and abbreviations, and the references, which are fully given, are to original sources. The book is attractively bound. BERNARD H. SMITH.

KLEINES HANDWÖRTERBUCH DER AGRICULTURCHEMIE. Von MAX PASSON. Leipzig: Wilhelm Engelmann. 1910. Pt. 1, pp. 454; Pt. 2, pp. 415. Unbound, M. 22; bound, M. 25.

The author recognizes in the preface that there are already plenty of books dealing with agricultural analytical methods, also with matters relating to the morphology and recognition of various plant products, and publications supplying the information necessary in answering questions likely to be raised by those engaged in farming. The object was not to attempt to duplicate or pattern after any of these works, but rather to bring together from various sources such information as gave promise of placing within reasonably small compass the information which a student of agricultural chemistry would be most likely to need. He has endeavored also to render available matter bearing upon a multitude of questions which those connected with agricultural experiment stations are continually being called upon to answer, and which might otherwise involve a search of many volumes.

The book not only meets such needs but also serves the purpose, for the student in this country, of a German agricultural technical lexicon wherein may be found certain terms common in German works but frequently not defined and unfamiliar to those whose acquaintance with technical German is limited. Perhaps as typical illustrations of the latter, one might mention "Hochmoorboden," "Niederungsmoor" and "Ammoniaksuperphosphat."

The work contains material relating to the more important soil-forming minerals, soils, soil amendments, fertilizers, products of plant life, etc., together with methods for the examination and quantitative determination of many of the more important substances of an agricultural nature and origin. It contains many illustrations, some of which are taken from an earlier well-known work by König, and from other sources.

In the selection of material the author has unfortunately confined himself closely to German sources and might have made the work more valuable and complete had he drawn in some instances on material available elsewhere in Europe, as well as in Japan and the United States. H. J. WHEELER.

PRODUCER GAS-FIRED FURNACES. By OSKAR NAGEL, PH.D., Consulting Chemical Engineer. New York: Oskar Nagel, P. O. Box 385. pp. 192. Price, $2.

This deals exhaustively with the production of producer

gas—the construction of producers, the combustion of the gas, and its application to the industries. This includes bone-black, gas retort, muffle, roasting, reverberatory, crucible, and enameling furnaces; in addition to these, the specific applications of producer gas to the iron and steel, the copper and zinc, the lime and cement, and glass industries are carefully discussed. Lastly there is a useful chapter on refractories used in these various furnaces.

The book is profusely illustrated—enough to give a good idea of the various furnaces, but hardly more—and is a valuable contribution to the literature and should be owned by all interested in the subject.

A. H. GILL.

DIE ELEKTROMOTORISCHEN KRÄFTE DER POLARISATION, UND IHRE MESSUNG MIT HILFE DES OSZILLOGRAPHEN. Von M. LE BLANC. Abhandlungen der Deutschen Bunsen Gesellschaft für angewandte physikalische Chemie. Halle, a/S.: Verlag von Wilhelm Knapp. 1910. pp. 79. Preis, m. 3.00; für mitglieder, m. 1.50.

The earlier work of LeBlanc on the electromotive force of polarization, or "decomposition values" of acids, bases and salts, is one of the most important contributions to physical chemistry in the nineties. It was this work which showed the untenability of the theory of electrolysis which held sway for more than a half century.

This investigation not only pointed out that the old theory of electrolysis contained within itself a self-evident contradiction, but also gave us a satisfactory theory in terms of which the facts in connection with the decomposition of acids, bases and salts by the current could be interpreted. Indeed, it went farther and furnished us with the experimental proof of the new theory of electrolysis—a proof so comprehensive and convincing as scarcely to have been questioned in recent years.

LeBlanc has now extended these earlier investigations, using the oscillograph to measure electromotive force.

H. C. J.